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Multicomponent superabsorbent gel particles

Abstract:

Multicomponent superabsorbent gel particles are disclosed. The multicomponent particles comprise at 3a9

least one acidic water-absorbing resin and at least one basic water-absorbing resin. Each particle contains at least one microdomain of the acidic resin in contact with, or in close proximity to, at least one microdomain of the basic resin. Blends of multicomponent superabsorbent gel particles with particles of a second water-absorbing resin also are disclosed. Improved diaper cores containing particles of the multicomponent superabsorbent gel particles also are disclosed

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(54) Title: MULTICOMPONENT SUPERABSORBENT GEL PARTICLES

(57) Abstract

Multicomponent superabsorbent gel particles are disclosed. The multicomponent particles comprise at least one acidic water-absorbing resin and at least one basic water-absorbing resin. Each particle contains at least one microdomain of the acidic resin in contact with, or in close proximity to, at least one microdomain of the basic resin. Blends of multicomponent superabsorbent gel particles with particles of a second water-absorbing resin also are disclosed. Improved diaper cores containing particles of the multicomponent super-absorbent gel particles also are disclosed.

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MULTICOMPONENT SUPERABSORBENT GEL PARTICLES

CROSS REFERENCE TO RELATED APPLICATIONS

This is a continuation-in-part of U.S. patent application Serial No. 09/120,674, filed July 22, 1998, pending, which is a continuation-in-part of U.S. patent application Serial No. 08/974,125, filed November 19, 1997, pending.

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FIELD OF THE INVENTION

The present invention relates to multicomponent superabsorbent gel particles containing at
least one acidic water-absorbing resin and at least
one basic water-absorbing resin. Each superabsorbent gel particle has at least one microdomain of
the acidic resin in contact with, or in close proximity to, at least one microdomain of the basic
resin. The present invention also relates to mixtures containing (a) multicomponent superabsorbent
particles, and (b) particles of an acidic waterabsorbing resin, a basic water-absorbing resin, or a
mixture thereof.

BACKGROUND OF THE INVENTION

Water-absorbing resins are widely used in sanitary goods, hygienic goods, wiping cloths, water-retaining agents, dehydrating agents, sludge coagulants, disposable towels and bath mats, disposable door mats, thickening agents, disposable litter

mats for pets, condensation-preventing agents, and release control agents for various chemicals. Water-absorbing resins are available in a variety of chemical forms, including substituted and unsubstituted natural and synthetic polymers, such as hydrolysis products of starch acrylonitrile graft polymers, carboxymethylcellulose, crosslinked polyacrylates, sulfonated polystyrenes, hydrolyzed polyacrylamides, polyvinyl alcohols, polyethylene oxides, polyvinylpyrrolidones, and polyacrylonitriles.

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"superabsorbent polymers," or SAPs, and typically are lightly crosslinked hydrophilic polymers. SAPs are generally discussed in Goldman et al. U.S. Patent Nos. 5,669,894 and 5,559,335, the disclosures of which are incorporated herein by reference. SAPs can differ in their chemical identity, but all SAPs are capable of absorbing and retaining amounts of aqueous fluids equivalent to many times their own weight, even under moderate pressure. For example, SAPs can absorb one hundred times their own weight, or more, of distilled water. The ability to absorb aqueous fluids under a confining pressure is an important requirement for an SAP used in a hygienic article, such as a diaper.

As used here and hereafter, the term "SAP particles" refers to superabsorbent polymer particles in the dry state, i.e., particles containing from no water up to an amount of water less than the weight of the particles. The terms "SAP gel" or "SAP hydrogel" refer to a superabsorbent polymer in the hydrated state, i.e., particles that have ab-

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sorbed at least their weight in water, and typically several times their weight in water.

The dramatic swelling and absorbent properties of SAPs are attributed to (a) electrostatic repulsion between the charges along the polymer chains, and (b) osmotic pressure of the counter ions. It is known, however, that these absorption properties are drastically reduced in solutions containing electrolytes, such as saline, urine, and blood. The polymers function much less effectively in the presence of such physiologic fluids.

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The decreased absorbency of electrolytecontaining liquids is illustrated by the absorption properties of a typical, commercially available SAP, i.e., sodium polyacrylate, in deionized water and in 15 0.9% by weight sodium chloride (NaCl) solution. The sodium polyacrylate can absorb 146.2 grams (g) of deionized water per gram of SAP (g/g) at 0 psi, 103.8 g of deionized water per gram of polymer at 0.28 psi, and 34.3 g of deionized water per gram of 20 polymer of 0.7 psi. In contrast, the same sodium polyacrylate is capable of absorbing only 43.5 g, 29.7 g, and 24.8 g of 0.9% aqueous NaCl at 0 psi, 0.28 psi, and 0.7 psi, respectively. The absorption capacity of SAPs for body fluids, such as urine or 25 menses, therefore, is dramatically lower than for deionized water because such fluids contain electrolytes. This dramatic decrease in absorption is termed "salt poisoning."

The salt poisoning effect has been explained as follows. Water-absorption and water-retention characteristics of SAPs are attributed to

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the presence of ionizable functional groups in the polymer structure. The ionizable groups typically are carboxyl groups, a high proportion of which are in the salt form when the polymer is dry, and which undergo dissociation and solvation upon contact with water. In the dissociated state, the polymer chain contains a plurality of functional groups having the same electric charge and, thus, repel one another. This electronic repulsion leads to expansion of the polymer structure, which, in turn, permits further absorption of water molecules. Polymer expansion, however, is limited by the crosslinks in the polymer structure, which are present in a sufficient number to prevent solubilization of the polymer.

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It is theorized that the presence of a significant concentration of electrolytes interferes with dissociation of the ionizable functional groups, and leads to the "salt poisoning" effect. Dissolved ions, such as sodium and chloride ions, therefore, have two effects on SAP gels. The ions screen the polymer charges and the ions eliminate the osmotic imbalance due to the presence of counter ions inside and outside of the gel. The dissolved ions, therefore, effectively convert an ionic gel into a nonionic gel, and swelling properties are lost.

The most commonly used SAP for absorbing electrolyte-containing liquids, such as urine, is neutralized polyacrylic acid, i.e., containing at least 50%, and up to 100%, neutralized carboxyl groups. Neutralized polyacrylic acid, however, is susceptible to salt poisoning. Therefore, to pro-

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vide an SAP that is less susceptible to salt poisoning, either an SAP different from neutralized polyacrylic acid must be developed, or the neutralized polyacrylic acid must be modified or treated to at least partially overcome the salt poisoning effect.

The removal of ions from electrolyte-containing solutions is often accomplished using ion exchange resins. In this process, deionization is performed by contacting an electrolyte-containing solution with two different types of ion exchange resins, i.e., an anion exchange resin and a cation exchange resin. The most common deionization procedure uses an acid resin (i.e., cation exchange) and a base resin (i.e., anion exchange). The two-step reaction for deionization is illustrated with respect to the desalinization of water as follows:

 $NaCl + R-SO_3H - R-SO_3Na + HCl$ $HCl + R-N(CH_3)_3OH - R-N(CH_3)_3Cl + H_2O.$

The acid resin (R-SO₃H) removes the sodium ion; and the base resin (R-N(CH₃)₃OH) removes the chloride ions. This ion exchange reaction, therefore, produces water as sodium chloride is adsorbed onto the resins. The resins used in ion exchange do not absorb significant amounts of water.

The most efficient ion exchange occurs when strong acid and strong base resins are employed. However, weak acid and weak base resins also can be used to deionize saline solutions. The efficiency of various combinations of acid and base exchange resins are as follows:

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Strong acid--strong base (most efficient)
Weak acid--strong base
Strong acid--weak base
Weak acid--weak base (least efficient).

The weak acid/weak base resin combination requires that a "mixed bed" configuration be used to obtain deionization. The strong acid/strong base resin combination does not necessarily require a mixed bed configuration to deionize water. Deionization also can be achieved by sequentially passing the electrolyte-containing solution through a strong acid resin and strong base resin.

A "mixed bed" configuration of the prior art is a physical mixture of an acid ion exchange resin and a base ion exchange resin in an ion ex-15 change column, as disclosed in Battaerd U.S. Patent No. 3,716,481. Other patents directed to ion exchange resins having one ion exchange resin imbedded in a second ion exchange resin are Hatch U.S. Patent No. 3,957,698, Wade et al. U.S. Patent No. 20 4,139,499, Eppinger et al. U.S. Patent No. 4,229,545, and Pilkington U.S. Patent No. 4,378,439. Composite ion exchange resins also are disclosed in Hatch U.S. Patent Nos. 3,041,092 and 3,332,890, and Weiss U.S. Patent No. 3,645,922. 25

The above patents are directed to nonswelling resins that can be used to remove ions from aqueous fluids, and thereby provide purified water. Ion exchange resins used for water purification must not absorb significant amounts of water because resin swelling resulting from absorption can

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lead to bursting of the ion exchange containment column.

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Ion exchange resins or fibers also have been disclosed for use in absorbent personal care devices (e.g., diapers) to control the pH of fluids that reach the skin, as set forth in Berg et al., U.S. Patent No. 4,685,909. The ion exchange resin is used in this application to reduce diaper rash, but the ion exchange resin is not significantly water absorbent and, therefore, does not improve the absorption and retention properties of the diaper.

Ion exchange resins having a composite particle containing acid and base ion exchange particles embedded together in a matrix resin, or having acid and base ion exchange particles adjacent to one another in a particle that is free of a matrix resin are disclosed in B.A. Bolto et al., J. Polymer Sci.:Symposium No. 55, John Wiley and Sons, Inc. (1976), pages 87-94. The Bolto et al. publication is directed to improving the reaction rates of ion exchange resins for water purification and does not utilize resins that absorb substantial amounts of water.

other investigators have attempted to

counteract the salt poisoning effect and thereby
improve the performance of SAPs with respect to
absorbing electrolyte-containing liquids, such as
menses and urine. For example, Tanaka et al. U.S.
Patent No. 5,274,018 discloses an SAP composition

comprising a swellable hydrophilic polymer, such as
polyacrylic acid, and an amount of an ionizable
surfactant sufficient to form at least a monolayer

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of surfactant on the polymer. In another embodiment, a cationic gel, such as a gel containing quaternized ammonium groups and in the hydroxide (i.e., OH) form, is admixed with an anionic gel (i.e., a polyacrylic acid) to remove electrolytes from the solution by ion exchange. Quaternized ammonium groups in the hydroxide form are very difficult and time-consuming to manufacture, thereby limiting the practical use of such cationic gels.

Wong U.S. Patent No. 4,818,598 discloses the addition of a fibrous anion exchange material, such as DEAE (diethylaminoethyl) cellulose, to a hydrogel, such as a polyacrylate, to improve absorption properties. The ion exchange resin "pretreats" the saline solution (e.g., urine) as the solution flows through an absorbent structure (e.g., a diaper). This pretreatment removes a portion of the salt from the saline. The conventional SAP present in the absorbent structure then absorbs the treated saline more efficiently than untreated-saline. The 20. ion exchange resin, per se, does not absorb the saline solution, but merely helps overcome the "salt poisoning" effect.

WO 96/17681 discloses admixing discrete anionic SAP particles, such as polyacrylic acid, with discrete polysaccharide-based cationic SAP particles to overcome the salt poisoning effect. Similarly, WO 96/15163 discloses combining a cationic SAP having at least 20% of the functional groups in a basic (i.e., OH) form with a cationic exchange resin, i.e., a nonswelling ion exchange resin, having at least 50% of the functional groups

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in the acid form. WO 96/15180 discloses an absorbent material comprising an anionic SAP, e.g., a polyacrylic acid and an anion exchange resin, i.e., a nonswelling ion exchange resin.

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These references disclose combinations that attempt to overcome the salt poisoning effect. However, the references merely teach the admixture of two types of particles, and do not suggest a single particle containing at least one microdomain 10 of an acidic resin in contact, or in close proximity, with at least one microdomain of a basic resin. These references also do not teach a mixture of resin particles wherein one component of the mixture is particles of a multicomponent SAP.

It would be desirable to provide discrete SAP particles that exhibit exceptional water absorption and retention properties, especially with respect to electrolyte-containing liquids, and thereby overcome the salt poisoning effect. In addition, it would be desirable to provide discrete SAP particles that have an ability to absorb liquids quickly, demonstrate good fluid permeability and conductivity into and through the SAP particle, and have a high gel strength such that the hydrogel formed from the SAP particles does not deform or flow under an ap-25 plied stress or pressure, when used alone or in a mixture with other water-absorbing resins.

SUMMARY OF THE INVENTION

The present invention is directed to multicomponent SAPs comprising at least one acidic 30

water-absorbing resin, such as a polyacrylic acid, and at least one basic water-absorbing resin, such as poly(vinylamine), a polyethyleneimine, or a poly(dialkylaminoalkyl acrylamide) or a poly(dialkylaminoalkyl methacrylamide), hereafter collectively referred to as poly(dialkylaminoalkyl (meth)-acrylamides).

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More particularly, the present invention is directed to multicomponent SAP particles containing at least one discrete microdomain of at least one acidic water-absorbing resin in contact with; or in close proximity to, at least one microdomain of at least one basic water-absorbing resin. multicomponent SAP particles can contain a plurality of microdomains of the acidic water-absorbing resin and/or the basic water-absorbing resin dispersed throughout the particle. The acidic resin can be a strong or a weak acidic resin. Similarly, the basic resin can be a strong or a weak basic resin. A preferred SAP contains one or more microdomains of at least one weak acidic resin and one or more microdomains of at least one weak basic resin. The properties demonstrated by such preferred multicomponent SAP particles are unexpected because, in ion exchange applications, the combination of a weak acid and a weak base is the least effective of any combination of a strong or weak acid ion exchange resin with a strong or weak basic ion exchange resin.

Accordingly, one aspect of the present invention is to provide SAP particles that have a high absorption rate, have good permeability and gel

strength, overcome the salt poisoning effect, and demonstrate an improved ability to absorb and retain electrolyte-containing liquids, such as saline, blood, urine, and menses. The present SAP particles contain discrete microdomains of acidic and basic resin, and during hydration, the particles resist coalescence but remain fluid permeable.

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Another aspect of the present invention is to provide an SAP having improved absorption and retention properties compared to a conventional SAP, such as sodium polyacrylate. The present multicomponent SAP particles are produced by any method that positions a microdomain of an acidic waterabsorbing resin in contact with, or in close proximity to, a microdomain of a basic water-absorbing resin to provide a discrete particle. In one embodiment, the SAP particles are produced by coextruding an acidic water-absorbing hydrogel and a basic water-absorbing hydrogel to provide multicomponent SAP particles having a plurality of discrete microdomains of an acidic resin and a basic resin dispersed throughout the particle. Such SAP particles demonstrate improved absorption and retention properties, and permeability through and between particles compared to SAP compositions comprising a simple admixture of acidic resin particles and basic resin particles.

In another embodiment, the present multicomponent SAP particles can be prepared by admixing dry particles of a basic resin with a hydrogel of an acidic resin, then extruding the resulting mixture to form multicomponent SAP parti-

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cles having microdomains of a basic resin dispersed throughout a continuous phase of an acidic resin. Alternatively, dry acidic resin particles can be admixed with a basic resin hydrogel, followed by extruding the resulting mixture to form multicomponent SAP particles having microdomains of an acidic resin dispersed in a continuous phase of a basic resin.

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In addition, a multicomponent SAP particle containing microdomains of an acidic resin and a basic resin dispersed in a continuous phase of a matrix resin can be prepared by adding dry particles of the acidic resin and dry particles of the basic resin to a hydrogel of the matrix hydrogel, then extruding. Other forms of the present multicomponent SAP particles, such as agglomerated particles, interpenetrating polymer network forms, laminar forms, and concentric sphere forms, also demonstrate improved fluid absorption and retention properties.

In accordance with yet another important aspect of the present invention, the acidic and basic resins are lightly crosslinked, such as with a suitable polyfunctional vinyl polymer. In preferred embodiments, the acidic resin, the basic resin, and/or the entire multicomponent SAP particle are surface treated or annealed to further improve water absorption and retention properties, especially under a load.

Yet another important feature of the pres-30 ent invention is to provide an SAP particle containing at least one microdomain of a weak acidic water-

absorbing resin in contact with at least one microdomain of a weak basic water-absorbing resin.

An example of a weak acid resin is polyacrylic acid having 0% to 25% neutralized carboxylic acid groups (i.e., DN=0 to DN=25). Examples of weak basic water-absorbing resins are a poly(vinylamine), a polyethylenimine, and a poly(dialkylaminoalkyl (meth)acrylamide) prepared from a monomer either having the general structure formula (I)

$$R_1 \xrightarrow{C=C} R_2$$

$$C-NH-(Y)-N$$

$$R_4$$

(I)

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$$R_1 = C = C$$

$$C = C$$

$$C = C$$

$$C = C$$

$$R_2$$

$$C = C$$

$$C = C$$

$$R_3$$

$$R_4$$

(II)

wherein R_1 and R_2 , independently, are selected from the group consisting of hydrogen and methyl, Y is a divalent straight chain or branched organic radical

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having 1 to 8 carbon atoms, and R_3 and R_4 , independently, are alkyl radicals having 1 to 4 carbon atoms. Examples of a strong basic water-absorbing resin are poly(vinylguanidine) and poly(allyl-quanidine).

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Yet another aspect of the present invention is to provide an improved SAP material comprising a combination containing (a) multicomponent SAP particles, and (b) particles of a second water-absorbing resin selected from the group consisting of an acidic water-absorbing resin, a basic water-absorbing resin, and a mixture thereof. The combination contains about 10% to about 90%, by weight, multicomponent SAP particles and about 10% to about 90%, by weight, particles of the second water-absorbing resin.

Still another aspect of the present invention is to provide diapers having a core comprising multicomponent SAP particles or an SAP material of the present invention.

These and other aspects and advantages of the present invention will become apparent from the following detailed description of the preferred embodiments.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic diagram of a waterabsorbing particle containing microdomains of a first resin dispersed in a continuous phase of a second resin;

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FIG. 2 is a schematic diagram of a waterabsorbing particle containing microdomains of a first resin and microdomains of a second resin dispersed throughout the particle;

FIGS. 3A and 3B are schematic diagrams of a water-absorbing particle having a core microdomain of a first resin surrounded by a layer of a second resin;

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FIGS. 4A-D are schematic diagrams of

water-absorbing particles having a microdomain of a

first resin in contact with a microdomain of a second resin;

FIGS. 5A and 5B are schematic diagrams of a water-absorbing particle having an interpenetrating network of a first resin and a second resin;

FIG. 6 contains plots of absorbance (in grams of synthetic urine per gram of multicomponent SAP particles) vs. annealing temperature for a one-hour annealing step;

FIG. 7 contains a plot of absorbance (in grams of synthetic urine per gram of multicomponent SAP particles) vs. time for an annealing step performed at 125°C;

FIGS. 8 and 9 contain plots of PUP at 0.7 psi (in g/g) vs. time (hrs) for present multicomponent SAP particles and prior art SAPs;

FIGS. 10 and 11 contain plots for initial Performance Under Pressure (PUP) capacity vs. the for present multicomponent SAP particles and prior art SAPs:

FIG. 12 contains plots of absorbance (in g/g) vs. weight percent of poly(AA) (DN=70) in a

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blend of multicomponent SAP particles and particles of poly(AA) (DN=70);

FIG. 13 contains plots of absorbance (in g/g) vs. weight percent of poly(AA) (DN=70) in a blend of particles of poly(AA) (DN=70), particles of poly(AA) (DN=0), and particles of poly(vinylamine);

FIGS. 14-17 are plots of absorbance (in g/g) vs. time (minutes) for a variety of blends of superabsorbent particles;

FIG. 18 is a plot of PUP at 0.7 psi vs. time (hrs) for a superabsorbent material containing 25% multicomponent SAP particles and 75% poly(AA) - (DN=70), by weight;

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FIG. 19 is a plot of initial PUP capacity vs. $t^{1/2}$ for a superabsorbent material containing 25% multicomponent SAP particles and 75% poly(AA) - (DN=70), by weight;

FIGS. 20, 21, 23-26, and 28 are plots of acquisition time (seconds) vs. number of insults for a series of laboratory prepared diaper cores under a load of 0.7 psi;

FIGS. 22, 27, and 29 are plots of acquisition rate vs. number of insults for a series of laboratory prepared diaper cores under a load of 0.7 psi.

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DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is directed to multicomponent SAP particles containing at least one microdomain of an acidic water-absorbing resin in close proximity to, and preferably in contact with, at least one microdomain of a basic water-absorbing resin. Each particle contains one or more microdomains of an acidic resin and one or more microdomains of a basic resin. The microdomains can be distributed nonhomogeneously or homogeneously throughout each particle.

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Each multicomponent SAP particle of the present invention contains at least one acidic water-absorbing resin and at least one basic water-absorbing resin. In one embodiment, the SAP particles consist essentially of acidic resins and basic resins, and contain microdomains of the acidic and/or basic resins. In another embodiment, microdomains of the acidic and basic resins are dispersed in an absorbent matrix resin.

The multicomponent SAP particles of the present invention are not limited to a particular structure or shape. However, it is important that substantially each SAP particle contain at least one microdomain of an acidic water-absorbing resin and at least one microdomain of a basic water-absorbing resin in close proximity to one another. Improved water absorption and retention, and improved fluid permeability through and between SAP particles, are observed as long as the acidic resin microdomain and the basic resin microdomain are in close proximity

within the particle. In a preferred embodiment, the microdomains of acidic and basic resin are in contact.

In some embodiments, an idealized multicomponent SAP particle of the present invention is analogous to a liquid emulsion wherein small droplets of a first liquid, i.e., the dispersed phase, are dispersed in a second liquid, i.e., the continuous phase. The first and second liquids are immiscible, and the first liquid, therefore, is homogeneously dispersed in the second liquid. The first liquid can be water or oil based, and conversely, the second liquid is oil or water based, respectively.

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Therefore, in one embodiment, the multicomponent SAP particles of the present invention can
be envisioned as one or more microdomains of an
acidic resin dispersed in a continuous phase of a
basic resin, or as one or more microdomains of a
basic resin dispersed in a continuous acid resin.
These idealized multicomponent SAP particles are
illustrated in FIG. 1 showing an SAP particle 10
having discrete microdomains 14 of a dispersed resin
in a continuous phase of a second resin 12. If
microdomains 14 comprise an acidic resin, then
continuous phase 12 comprises a basic resin. Conversely, if microdomains 14 comprise a basic resin,
then continuous phase 12 is an acidic resin.

In another embodiment, the SAP particles

are envisioned as microdomains of an acidic resin

and microdomains of a basic resin dispersed throughout each particle, without a continuous phase. This

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embodiment is illustrated in FIG. 2, showing an idealized multicomponent SAP particle 20 having a plurality of microdomains of an acidic resin 22 and a plurality of microdomains of a basic resin 24 dispersed throughout particle 20.

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In yet another embodiment, microdomains of the acidic and basic resins are dispersed throughout a continuous phase comprising a matrix resin. This embodiment also is illustrated in FIG. 1 wherein multicomponent SAP particle 10 contains one or more microdomains 14, each an acidic resin or a basic resin, dispersed in a continuous phase 12 of a matrix resin.

It should be understood that the microdomains within each particle can be of regular or
irregular shape, and that the microdomains can be
dispersed homogeneously or nonhomogeneously
throughout each particle. Accordingly, another
embodiment of the SAP particles is illustrated in
FIG. 3A, showing an idealized multicomponent particle 30 having a core 32 of an acidic water-absorbing
resin surrounded by a shell 34 of a basic waterabsorbing resin. Conversely, core 32 can comprise a
basic resin, and shell 34 can comprise an acidic
resin.

FIG. 3B illustrates a similar embodiment having a core and concentric shells that alternate between shells of acidic resin and basic resin. In one embodiment, core 42 and shell 46 comprise an acidic water-absorbing resin, and shell 44 comprises a basic water-absorbing resin. Other embodiments include: core 42 and shell 46 comprising a basic

resin and shell 44 comprising an acidic resin, or core 42 comprising a matrix resin and shells 44 and 46 comprising an acidic resin and a basic resin in alternating shells. Other configurations are apparent to persons skilled in the art, such as increasing the number of shells around the core.

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FIGS. 4A and 4B illustrate embodiments of the present SAP particles wherein one microdomain of an acidic water-absorbing resin (i.e., 52 or 62) is in contact with one microdomain of a basic water-absorbing resin (i.e., 54 or 64) to provide a multicomponent SAP particle (i.e., 50 or 60). In these embodiments, the microdomains are dispersed nonhomogeneously throughout the particle. bodiments illustrated in FIG. 4 extend to SAP particles having more than one microdomain of each of the acidic resin and the basic resin, as illustrated in FIGS. 4C and 4D, wherein multicomponent SAP particles 70 and 80 contain alternating zones of acidic water-absorbing resin (e.g., 72 or 82) and basic water-absorbing resin (e.g., 74 or 84). Particles 70 and 80 also can contain one or more layers 72, 74, 82, or 84 comprising a matrix resin.

In another embodiment, the multicomponent

SAP particle comprises an interpenetrating polymer
network (IPN), as illustrated in FIG. 5. An IPN is
a material containing two polymers, each in network
form. In an IPN, two polymers are synthesized
and/or crosslinked in the presence of one another,
and polymerization can be sequential or simultaneous. Preparation of a sequential IPN begins with
the synthesis of a first crosslinked polymer. Then,

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monomers comprising a second polymer, a crosslinker, and initiator are swollen into the first polymer, and polymerized and crosslinked in situ. For example, a crosslinked poly(acrylic acid) network can be infused with solution containing a poly(vinylamine) and a crosslinker.

Simultaneous IPNs are prepared using a solution containing monomers of both polymers and their respective crosslinkers, which then are polymerized simultaneously by noninterfering modes, such as stepwise or chain polymerizations. A third method of synthesizing IPNs utilizes two lattices of linear polymers, mixing and coagulating the lattices, and crosslinking the two components simultaneously. Persons skilled in the art are aware of other ways that an IPN can be prepared, each yielding a particular topology.

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In most IPNs, the polymer phases separate to form distinct zones of the first polymer and distinct zones of the second polymer. In the remaining IPNs, the first and second polymers remain "soluble" in one another. Both forms of IPN have microdomains, and are multicomponent SAPs of the present invention.

FIGS. 5A and 5B illustrate IPN systems.

FIG. 5A illustrates an IPN made by sequentially synthesizing the first and second polymers. FIG. 5B illustrates an IPN made by simultaneously polymerizing the first and second polymers. In FIGS. 5A and 5B, the solid lines represent the first polymer (e.g., the acidic polymer) and the lightly dotted lines represent the second polymer (e.g., the basic

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polymer). The heavy dots represent crosslinking sites.

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In another embodiment, the multicomponent SAP particles are agglomerated particles prepared from fine particles of an acidic water-absorbing resin and fine particles of a basic water-absorbing resin. Typically, a fine resin particle has a diameter of less than about 200 microns (p), such as about 0.01 to about 180 μ . The agglomerated multicomponent SAP particles are similar in structure to the particle depicted in FIG. 2. With respect to the agglomerated SAP particles, it is important that the particles have sufficient dry agglomeration (i.e., in the dry state) and wet agglomeration (i.e., in the hydrogel state) to retain single particle properties, i.e., the particles do not disintegrate into their constituent fine particles of acidic resin and basic resin.

In particular, the agglomerated particles 20 have sufficient dry agglomeration to withstand fracturing. The dry agglomerated particles typically have an elastic character and, therefore, are not friable. The agglomerated particles also have sufficient wet strength to exhibit a property termed 25 "wet agglomeration." Wet agglomeration is defined as the ability of an agglomerated multicomponent SAP particle to retain its single particle nature upon hydration, i.e., a lack of deagglomeration upon hydration. Wet agglomeration is determined by posi-30 tioning fifty agglomerated SAP particles on a watch glass and hydrating the particles with 20 times their weight of a 1% (by weight) sodium chloride

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solution (i.e., 1% saline). The particles are spaced sufficiently apart such that they do not contact one another after absorbing the saline and swelling. The SAP particles are allowed to absorb the saline solution for one hour, then the number of SAP particles is recounted under a microscope. The multicomponent SAP particles pass the wet agglomeration test if no more than about 53 hydrated particles are counted.

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The multicomponent SAP particles of the present invention therefore comprise an acidic resin and a basic resin in a weight ratio of about 90:10 to about 10:90, and preferably about 20:80 to about 80:20. To achieve the full advantage of the present invention, the weight ratio of acidic resin to basic resin in a multicomponent SAP particle is about 30:70 to about 70:30. The acidic and basic resins can be distributed homogeneously or nonhomogeneously throughout the SAP particle.

The present multicomponent SAP particles contain at least about 50%, and preferably at least about 70%, by weight of acidic resin plus basic resin. To achieve the full advantage of the present invention, a multicomponent SAP particle contains about 80% to 100% by weight of the acidic resin plus basic resin. Components of the present SAP particles, other than the acidic and basic resin, typically, are matrix resins or other minor optional ingredients.

The multicomponent SAP particles of the present invention can be in any form, either regular or irregular, such as granules, fibers, beads, pow-

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ders, flakes, or foams, or any other desired shape, such as a sheet of the multicomponent SAP. In embodiments wherein the multicomponent SAP is prepared using an extrusion step, the shape of the SAP is determined by the shape of the extrusion die. The shape of the multicomponent SAP particles also can be determined by other physical operations, such as milling or by the method of preparing the particles, such as agglomeration.

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In one preferred embodiment, the present SAP particles are in the form of a granule or a bead, having a particle size of about 10 to about 10,000 microns (µm), and preferably about 100 to about 1,000 µm. To achieve the full advantage of the present invention, the multicomponent SAP particles have a particle size of about 150 to about 800 µm.

A microdomain is defined as a volume of an acidic resin or a basic resin that is present in a multicomponent SAP particle. Because each multicomponent SAP particle contains at least one microdomain of an acidic resin, and at least one microdomain of a basic resin, a microdomain has a volume that is less than the volume of the multicomponent SAP particle. A microdomain, therefore, can be as large as about 90% of the volume of multicomponent SAP particles.

Typically, a microdomain has a diameter of about 750 µm or less, and preferably about 100 µm or less. To achieve the full advantage of the present invention, a microdomain has a diameter of about 20 µm or less. The multicomponent SAP particles also

contain microdomains that have submicron diameters, e.g., microdomain diameters of less than 1 μm , preferably less than 0.1 μm , to about 0.01 μm .

In another preferred embodiment, the multicomponent SAP particles are in the shape of a 5 fiber, i.e., an elongated, acicular SAP particle. The fiber can be in the shape of a cylinder, for example, having a minor dimension (i.e., diameter) and a major dimension (i.e., length). The fiber also can be in the form of a long filament that can 10 be woven. Such filament-like fibers have a weight of below about 80 decitex, and preferably below about 70 decitex, per filament, for example, about 2 to about 60 decitex per filament. Tex is the weight in grams per one kilometer of fiber. One tex equals 15 10 decitex. For comparison, poly(acrylic acid) is about 4 decitex, and poly(vinylamine) is about 80 decitex.

a minor dimension (i.e., diameter of the fiber) less than about 1 mm, usually less than about 500 μ m, and preferably less than 250 μ m, down to about 50 μ m. The cylindrical SAP fibers can have a relatively short major dimension, for example, about 1 mm, e.g., in a fibrid, lamella, or flake-shaped article, but generally the fiber has a length of about 3 to about 100 mm. The filament-like fibers have a ratio of major dimension to minor dimension of at least 500 to 1, and preferably at least 1000 to 1, for example, up to and greater than 10,000 to 1.

Each multicomponent SAP particle contains one or more microdomains of an acidic water-absorb-

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ing resin and one or more microdomains of a basic water-absorbing resin, either in contact or in close proximity to one another. As illustrated hereafter, the microdomain structure of the present SAP particles provides improved fluid absorption (both in amount of fluid absorbed and retained, and rate of absorption) compared to an SAP comprising a simple mixture of discrete acidic SAP resin particles and discrete basic SAP resin particles. In accordance with another important feature of the present invention, the present multicomponent SAP particles also demonstrated improved permeability, both through an individual particle and between particles. present SAP particles, therefore, have an improved ability to rapidly absorb a fluid, even in "gush" situations, for example, when used in diapers to absorb urine.

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The features of good permeability, absorption and retention properties, especially of electrolyte-containing liquids, demonstrated by the present multicomponent SAP particles, is important with respect to practical uses of an SAP. These improved properties are attributed, in part, to the fact that electrolyte removal from the liquid is facilitated by contacting a single particle (which, in effect, performs an essentially simultaneous deionization of the liquid), as opposed to the liquid having to contact individual acidic and basic particles (which, in effect, performs a sequential two-step deionization).

If a blend of acidic resin particles and basic resin particles is used, the particles

typically have a small particle size. A small particle size is required to obtain desirable desalination kinetics, because the electrolyte is removed in a stepwise manner, with the acidic resin removing the cation and the basic resin removing the anion. The electrolyte-containing fluid, therefore, must contact two particles for desalination, and this process is facilitated by small particle sized SAPs. Small particles, however, have the effect of reducing flow of the fluid through and between SAP particles, i.e., permeability is reduced and a longer time is required to absorb the fluid.

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In addition, in practical use, such as in diapers, SAPs are used in conjunction with a cellulosic pulp. If a blend of acidic resin particles and basic resin particles is used as the SAP, the cellulosic pulp can cause a separation between the acidic resin particles and basic resin particles, which adversely affects desalination. The present multidomain composites overcome this problem because the acidic resin and basic resin are present in a single particle. The introduction of cellulosic pulp, therefore, cannot separate the acidic and basic resin and cannot adversely affect desalination by the SAP.

A single multicomponent SAP particle simultaneously desalinates an electrolyte-containing liquid. Desalination is essentially independent of particle size. Accordingly, the present multicomponent SAP particles can be of a larger size. These features allow for improved liquid permeability through and between the SAP particles, and re-

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sults in a more rapid absorption of the electrolytecontaining liquid.

The following schematic reactions illustrate the reactions which occur to deionize, e.g., desalinate, an aqueous saline solution, and that are performed essentially simultaneously in a single microcomposite SAP particle, but are performed stepwise in a simple mixture of acidic and basic resins:

R-CO₂H + NaCl - R-CO₂-Na⁺ + HCl

10 (acidic resin)

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 $R-NH_2 + HCl - R-NH_3^*Cl^-$ (basic resin).

The present multicomponent SAP particle, can be in a form wherein a microdomain of an acidic water-absorbing resin is in contact with a microdomain of a basic water-absorbing resin. In another embodiment, the SAP particles can be in a form wherein at least one microdomain of an acidic waterabsorbing resin is dispersed in a continuous phase of a basic water-absorbing resin. Alternatively, the multicomponent SAP can be in a form wherein at least one microdomain of a basic resin is dispersed in a continuous phase of an acidic resin. other embodiment, at least one microdomain of one or more acidic resin and at least one microdomain of one or more basic resin comprise the entire SAP particle, and neither type of resin is considered the dispersed or the continuous phase. In yet another embodiment, at least one microdomain of an acidic resin and at least one microdomain of a basic resin are dispersed in a matrix resin.

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An acidic water-absorbing resin present in a multicomponent SAP particle can be either a strong or a weak acidic water-absorbing resin. The acidic water-absorbing resin can be a single resin, or a mixture of resins. The acidic resin can be a homopolymer or a copolymer. The identity of the acidic water-absorbing resin is not limited as long as the resin is capable of swelling and absorbing at least ten times its weight in water, when in a neutralized form. The acidic resin is present in its acidic form, i.e., about 75% to 100% of the acidic moieties are present in the free acid form. As illustrated hereafter, although the free acid form of a acidic water-absorbing resin is generally a poor water 15 absorbent, the combination of an acidic resin and a basic resin in a present multicomponent SAP particle provides excellent water absorption and retention properties.

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The acidic water-absorbing resin typically is a lightly crosslinked acrylic-type resin, such as 20 lightly crosslinked polyacrylic acid. The lightly crosslinked acidic resin typically is prepared by polymerizing an acidic monomer containing an acyl moiety, e.g., acrylic acid, or a moiety capable of providing an acid group, i.e., acrylonitrile, in the 25 presence of a crosslinker, i.e., a polyfunctional organic compound. The acidic resin can contain other copolymerizable units, i.e., other monoethylenically unsaturated comonomers, well known in the art, as long as the polymer is substantially, i.e., 30 at least 10%, and preferably at least 25%, acidic monomer units. To achieve the full advantage of the

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present invention, the acidic resin contains at least 50%, and more preferably, at least 75%, and up to 100%, acidic monomer units. The other copolymerizable units can, for example, help improve the hydrophilicity of the polymer.

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Ethylenically unsaturated carboxylic acid and carboxylic acid anhydride monomers useful in the acidic water-absorbing resin include acrylic acid, methacrylic acid, ethacrylic acid, α -chloroacrylic acid, α -cyanoacrylic acid, β -methylacrylic acid (crotonic acid), α -phenylacrylic acid, β -acryloxy-propionic acid, sorbic acid, α -chlorosorbic acid, angelic acid, cinnamic acid, p-chlorocinnamic acid, β -stearylacrylic acid, itaconic acid, citraconic acid, mesaconic acid, glutaconic acid, aconitic acid, maleic acid, furmaric acid, tricarboxyethylene, and maleic anhydride.

Ethylenically unsaturated sulfonic acid monomers include aliphatic or aromatic vinyl sulfonic acids, such as vinylsulfonic acid, allyl sulfonic acid, vinyl toluene sulfonic acid, styrene sulfonic acid, acrylic and methacrylic sulfonic acids, such as sulfoethyl acrylate, sulfoethyl methacrylate, sulfopropyl acrylate, sulfopropyl methacrylate, 2-hydroxy-3-methacryloxypropyl sulfonic acid, and 2-acrylamide-2-methylpropane sulfonic acid.

As set forth above, polymerization of acidic monomers, and copolymerizable monomers, if present, most commonly is performed by free radical processes in the presence of a polyfunctional organic compound. The acidic resins are crosslinked

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to a sufficient extent such that the polymer is water insoluble. Crosslinking renders the acidic resins substantially water insoluble, and, in part, serves to determine the absorption capacity of the resins. For use in absorption applications, an acidic resin is lightly crosslinked, i.e., has a crosslinking density of less than about 20%, preferably less than about 10%, and most preferably about 0.01% to about 7%.

10 A crosslinking agent most preferably is
used in an amount of less than about 7 wt%, and
typically about 0.1 wt% to about 5 wt%, based on the
total weight of monomers. Examples of crosslinking
polyvinyl monomers include, but are not limited to,
15 polyacrylic (or polymethacrylic) acid esters represented by the following formula (III); and bisacrylamides, represented by the following formula (IV).

$$\begin{array}{c|c}
CH_2=CH & HC=CH_2 \\
C=C-O-X & O-C=O
\end{array}$$

(III)

wherein x is ethylene, propylene, trimethylene, 20 cyclohexyl, hexamethylene, 2-hydroxypropylene, -(CH₂CH₂O)_nCH₂CH₂-, or

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n and m are each an integer 5 to 40, and k is 1 or 2;

$$CH_2$$
= CH
 HC = CH_2
 O = C - NH (CH_2CH_2NH) $_1C$ = O

(IV)

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wherein 1 is 2 or 3.

The compounds of formula (III) are prepared by reacting polyols, such as ethylene glycol, propylene glycol, trimethylolpropane, 1,6-hexanediol, glycerin, pentaerythritol, polyethylene glycol, or polypropylene glycol, with acrylic acid or methacrylic acid. The compounds of formula (IV) are obtained by reacting polyalkylene polyamines, such as diethylenetriamine and triethylenetetramine, with acrylic acid.

Specific crosslinking monomers include, but are not limited to, 1,4-butanediol diacrylate, 1,4-butanediol dimethacrylate, 1,3-butylene glycol diacrylate, 1,3-butylene glycol dimethacrylate, diethylene glycol diacrylate, diethylene glycol dimethacrylate, ethoxylated bisphenol A diacrylate, ethoxylated bisphenol A dimethacrylate, ethylene glycol dimethacrylate, 1,6-hexanediol diacrylate, 1,6-hexanediol dimethacrylate, neopentyl glycol

dimethacrylate, polyethylene glycol diacrylate, polyethylene glycol dimethacrylate, triethylene glycol diacrylate, triethylene glycol dimethacrylate, tripropylene glycol diacrylate, tetraethylene glycol diacrylate, tetraethylene glycol 5 dimethacrylate, dipentaerythritol pentaacrylate, pentaerythritol tetraacrylate, pentaerythritol triacrylate, trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, tris(2-hydroxyethyl)isocyanurate triacrylate, tris(2-hydroxyethyl)iso-10 cyanurate trimethacrylate, divinyl esters of a polycarboxylic acid, diallyl esters of a polycarboxylic acid, triallyl terephthalate, diallyl maleate, diallyl fumarate, hexamethylenebismaleimide, trivinyl trimellitate, divinyl adipate, diallyl succinate, a 15 divinyl ether of ethylene glycol, cyclopentadiene diacrylate, tetraallyl ammonium halides, or mixtures thereof. Compounds such as divinylbenzene and divinyl ether also can be used to crosslink the poly(dialkylaminoalkyl acrylamides). Especially 20 preferred crosslinking agents are N, N'-methylenebisacrylamide, N,N'-methylenebismethacrylamide, ethylene glycol dimethacrylate, and trimethylolpropane triacrylate.

The acidic resin, either strongly acidic or weakly acidic, can be any resin that acts as an SAP in its neutralized form. The acidic resins typically contain a plurality of carboxylic acid, sulfonic acid, phosphonic acid, phosphoric acid, and/or sulfuric acid moieties. Examples of acidic resins include, but are not limited to, polyacrylic acid, hydrolyzed starch-acrylonitrile graft copoly-

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mers, starch-acrylic acid graft copolymers, saponified vinyl acetate-acrylic ester copolymers, hydrolyzed acrylonitrile copolymers, hydrolyzed acrylamide copolymers, ethylene-maleic anhydride copolymers, isobutylene-maleic anhydride copolymers, poly(vinylsulfonic acid), poly(vinylphosphonic acid), poly(vinylphosphoric acid), poly(vinylphosphoric acid), poly(vinylphosphoric acid), sulfonated polystyrene, poly(aspartic acid), poly(lactic acid), and mixtures thereof. The preferred acidic resins are the polyacrylic acids.

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The multicomponent SAPs can contain individual microdomains that: (a) contain a single acidic resin or (b) contain more than one, i.e., a mixture, of acidic resins. The multicomponent SAPs also can contain microdomains wherein, for the acidic component, a portion of the acidic microdomains comprise a first acidic resin or acidic resin mixture, and the remaining portion comprises a second acidic resin or acidic resin mixture.

Analogous to the acidic resin, the basic water-absorbing resin in the present SAP particles can be a strong or weak basic water-absorbing resins. The basic water-absorbing resin can be a single resin or a mixture of resins. The basic resin can be a homopolymer or a copolymer. The identity of the basic resin is not limited as long as the basic resin is capable of swelling and absorbing at least 10 times its weight in water, when in a charged form. The weak basic resin typically is present in its free base, or neutral, form, i.e., about 75% to about 100% of the basic moieties, e.g., amino groups, are present in a neutral, uncharged

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form. The strong basic resins typically are present in the hydroxide (OH) or bicarbonate (HCO_3) form.

The basic water-absorbing resin typically is a lightly crosslinked acrylic type resin, such as a poly(vinylamine) or a poly(dialkylaminoalkyl (meth)acrylamide). The basic resin also can be a polymer such as a lightly crosslinked polyethylenimine, a poly(allylamine), a poly(allylamine), a poly(dimethyldiallylammonium hydroxide), a quaternized polystyrene derivative, such as

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a quanidine-modified polystyrene, such as

a quaternized poly((meth)acrylamide) or ester ana15 log, such as

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or

$$q$$
 $Q (CH_2)_n N^+ Me_3$ OH

wherein Me is methyl, R₂ is hydrogen or methyl, n is a number 1 to 8, and q is a number from 10 to about 100,000, or a poly(vinylguanidine), i.e., poly(VG), a strong basic water-absorbing resin having the general structural formula (V)

$$R_{5}$$
 R_{6}
 R_{6}

(V)

wherein q is a number from 10 to about 100,000, and R₅ and R₆, independently, are selected from the group consisting of hydrogen, C₁-C₄ alkyl, C₃-C₆ cycloalkyl, benzyl, phenyl, alkyl-substituted phenyl, naphthyl, and similar aliphatic and aromatic groups. The lightly crosslinked basic water-absorbing resin can

contain other copolymerizable units and is crosslinked using a polyfunctional organic compound, as set forth above with respect to the acidic waterabsorbing resin.

A basic water-absorbing resin used in the 5 present SAP particles typically contains an amino or a guanidino group. Accordingly, a water-soluble basic resin also can be crosslinked in solution by suspending or dissolving an uncrosslinked basic resin in an aqueous or alcoholic medium, then adding 10 a di- or polyfunctional compound capable of crosslinking the basic resin by reaction with the amino groups of the basic resin. Such crosslinking agents include, for example, multifunctional aldehydes (e.g., glutaraldehyde), multifunctional 15 acrylates (e.g., butanediol diacrylate, TMPTA), halohydrins (e.g., epichlorohydrin), dihalides (e.g., dibromopropane), disulfonate esters (e.g., $ZA(O_2)O-(CH_2)_n-OS(O)_2Z$, wherein n is 1 to 10, and Z is methyl or tosyl), multifunctional epoxies (e.g., 20 ethylene glycol diglycidyl ether), multifunctional esters (e.g., dimethyl adipate), multifunctional acid halides (e.g., oxalyl chloride), multifunctional carboxylic acids (e.g., succinic acid), carboxylic acid anhydrides (e.g., succinic anhy-25 dride), organic titanates (e.g., TYZOR AA from DuPont), melamine resins (e.g., CYMEL 301, CYMEL 303, CYMEL 370, and CYMEL 373 from Cytec Industries, Wayne, NJ), hydroxymethyl ureas (e.g., N,N'dihydroxymethyl-4,5-dihydroxyethyleneurea), and 30 multifunctional isocyanates (e.g., toluene diisocyanate or methylene diisocyanate). Crosslinking

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agents also are disclosed in Pinschmidt, Jr. et al. U.S. Patent No. 5,085,787, incorporated herein by reference, and in EP 450 923.

Conventionally, the crosslinking agent is water or alcohol soluble, and possesses sufficient reactivity with the basic resin such that crosslinking occurs in a controlled fashion, preferably at a temperature of about 25°C to about 150°C. Preferred crosslinking agents are ethylene glycol diglycidyl ether (EGDGE), a water-soluble diglycidyl ether, and a dibromoalkane, an alcohol-soluble compound.

The basic resin, either strongly or weakly basic, therefore, can be any resin that acts as an SAP in its charged form. The basic resin typically contains amino or guanidino moieties. Examples of basic resins include a poly(vinylamine), a polyethylenimine, a poly(vinylguanidine), a poly(allylamine), a poly(allylguanidine), or a poly(dialkylaminoalkyl (meth)acrylamide) prepared by polymerizing and lightly crosslinking a monomer having the structure

$$R_1 = C = C$$

$$C = NH - (Y) - N$$

$$R_4$$

or its ester analog

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$$R_1 = C - C - (Y) - N$$

$$R_2 = C - C - (Y) - N$$

$$R_3 = C - C - (Y) - N$$

wherein R₁ and R₂, independently, are selected from the group consisting of hydrogen and methyl, Y is a divalent straight chain or branched organic radical having 1 to 8 carbon atoms, and R₃ and R₄, independently, are alkyl radicals having 1 to 4 carbon atoms. Preferred basic resins include a poly(vinylamine), polyethylenimine, poly(vinylguanadine), poly(dimethylaminoethyl acrylamide) (poly(DAEA)), and poly(dimethylaminopropyl methacrylamide) (poly-(DMAPMA)). Analogous to microdomains of an acidic resin, the present multicomponent SAPs can contain microdomains of a single basic resin, microdomains containing a mixture of basic resins, or microdomains of different basic resins.

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The present multicomponent SAPs can be prepared by various methods. It should be understood that the exact method of preparing a multicomponent SAP is not limited by the following embodiments. Any method that provides a particle having at least one microdomain of an acidic resin in contact with or in close proximity to at least one microdomain of a basic resin is suitable.

In one method, dry particles of a basic

resin, optionally surface crosslinked and/or

annealed, are admixed into a rubbery gel of an acidic

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resin. The resulting mixture is extruded, then dried, and optionally surface crosslinked and/or annealed, to provide multicomponent SAP particles having microdomains of a basic resin dispersed in a continuous phase of an acidic resin. Alternatively, particles of an acidic resin, optionally surface crosslinked and/or annealed, can be admixed into a rubbery gel of a basic resin, and the resulting mixture is extruded and dried, and optionally surface crosslinked and/or annealed, to provide multicomponent SAP particles having microdomains of an acidic resin dispersed in a continuous phase of a basic resin.

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In another method, dry particles of an acidic resin can be admixed with dry particles of a basic resin, and the resulting mixture is formed into a hydrogel, then extruded, to form multicomponent SAP particles.

In yet another method, a rubbery gel of an acidic resin and a rubbery gel of a basic resin, each optionally surface crosslinked and/or annealed, are coextruded, and the coextruded product is dried, and optionally surface crosslinked and/or annealed, to form multicomponent SAP particles containing microdomains of the acidic resin and the basic resin dispersed throughout the particle.

The method of preparing the present multicomponent SAP particles, therefore, is not limited, and does not require an extrusion step. Persons skilled in the art are aware of other methods of preparation wherein the multicomponent SAP contains at least one microdomain of an acidic resin and at

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least one microdomain of a basic resin in contact or in close proximity with each other. One example is agglomeration of fine particles of at least one acidic resin and at least one basic resin with each other, and optionally a matrix resin, to provide a multicomponent SAP particle containing microdomains of an acidic and/or basic resin. The multicomponent SAP particles can be ground to a desired particle size, or can be prepared by techniques that yield the desired particle size. Other nonlimiting methods of preparing an SAP particle of the present invention are set forth in the examples.

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In embodiments wherein an acidic resin and a basic resin are present as microdomains within a matrix of a matrix resin, particles of an acidic resin and a basic resin are admixed with a rubbery gel of a matrix resin, and the resulting mixture is extruded, then dried, to form multicomponent SAP particles having microdomains of an acidic resin and a basic resin dispersed in a continuous phase of a matrix resin. Alternatively, rubbery gels of an acidic resin, basic resin, and matrix resin can be coextruded to provide a multicomponent SAP containing microdomains of an acidic resin, a basic resin, and a matrix resin dispersed throughout the particle. this embodiment, the acidic resin, basic resin, and resulting multicomponent SAP, each can be optionally surface crosslinked and/or annealed.

The matrix resin is any resin that allows

fluid transport such that a liquid medium can contact
the acidic and basic resin. The matrix resin typically is a hydrophilic resin capable of absorbing

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water. Nonlimiting examples of matrix resins include poly(vinyl alcohol), poly(N-vinylformamide), polyethylene oxide, poly(meth)acrylamide, poly(hydroxyethylacrylate), hydroxyethylcellulose, methylcellulose, and mixtures thereof. The matrix resin also can be a conventional water-absorbing resin, for example, a polyacrylic acid neutralized greater than 25 mole %, and typically greater than 50 mole %.

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In preferred embodiments, the acidic resin, the basic resin, and/or the multicomponent SAP particles are surface treated and/or annealed. Surface treatment and/or annealing results in surface crosslinking of the particle. In especially preferred embodiments, the acidic and/or basic resins comprising the multicomponent SAP particles are surface treated and/or annealed, and the entire multicomponent SAP particle is surface treated and/or annealed. It has been found that surface treating and/or annealing of an acidic resin, a basic resin, and/or a multicomponent SAP particle of the present invention enhances the ability of the resin or multicomponent SAP particle to absorb and retain aqueous media under a load.

Surface crosslinking is achieved by contacting an acidic resin, a basic resin, and/or a multicomponent SAP particle with a solution of a surface crosslinking agent to wet predominantly only the outer surfaces of the resin or SAP particle. Surface crosslinking and drying of the resin or multicomponent SAP particle then is performed, preferably by heating at least the wetted surfaces of the resin or multicomponent SAP particles.

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Typically, the resins and/or SAP particles are surface treated with a solution of a surface crosslinking agent. The solution contains about 0.01% to about 4%, by weight, surface crosslinking agent, and preferably about 0.4% to about 2%, by weight, surface crosslinking agent in a suitable solvent, for example, water or an alcohol. solution can be applied as a fine spray onto the surface of freely tumbling resin particles or multicomponent SAP particles at a ratio of about 1:0.01 to about 1:0.5 parts by weight resin or SAP particles to solution of surface crosslinking agent. The surface crosslinker is present in an amount of 0% to about 5%, by weight of the resin or SAP particle, and preferably 0% to about 0.5% by weight. achieve the full advantage of the present invention, the surface crosslinker is present in an amount of about 0.001% to about 0.1% by weight.

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The crosslinking reaction and drying of the surface-treated resin or multicomponent SAP particles are achieved by heating the surface-treated polymer at a suitable temperature, e.g., about 25°C to about 150°C, and preferably about 105°C to about 120°C. However, any other method of reacting the crosslinking agent to achieve surface crosslinking of the 25 resin or multicomponent SAP particles, and any other method of drying the resin or multicomponent SAP particles, such as microwave energy, or the such as, can be used.

With respect to the basic resin, or multicomponent SAP particles having a basic resin present on the exterior surface of the particles, suitable

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surface crosslinking agents include di- or polyfunctional molecules capable of reacting with amino groups and crosslinking a basic resin. Preferably, the surface crosslinking agent is alcohol or water soluble and possesses sufficient reactivity with a basic resin such that crosslinking occurs in a controlled fashion at a temperature of about 25°C to about 150°C.

Nonlimiting examples of suitable surface crosslinking agents for basic resins include:

(a) dihalides and disulfonate esters, for example, compounds of the formula

$$Y-(CH_2)_p-Y$$
,

wherein p is a number from 2 to 12, and Y, independently, is halo (preferably bromo), tosylate, mesylate, or other alkyl or aryl sulfonate esters;

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- (b) multifunctional aziridines;
- (c) multifunctional aldehydes, for example, glutaraldehyde, trioxane, paraformaldehyde, terephthaldehyde, malonaldehyde, and glyoxal, and acetals and bisulfites thereof;
 - (d) halohydrins, such as epichlorohydrin;
- (e) multifunctional epoxy compounds, for example, ethylene glycol diglycidyl ether, bisphenol A diglycidyl ether, and bisphenol F diglycidyl ether,
- (f) multifunctional carboxylic acids and esters, acid chlorides, and anhydrides derived therefrom, for example, di- and polycarboxylic acids containing 2 to 12 carbon atoms, and the methyl and ethyl esters, acid chlorides, and anhydrides derived therefrom, such as oxalic acid, adipic acid, succinic acid, dodecanoic acid, malonic acid, and glutaric

acid, and esters, anhydrides, and acid chlorides derived therefrom;

- (g) organic titanates, such as TYZOR AA, available from E.I. DuPont de Nemours, Wilmington, DE;
- (h) melamine resins, such as the CYMEL resins available from Cytec Industries, Wayne, NJ;

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- (i) hydroxymethyl ureas, such as N,N'-dihydroxymethyl-4,5-dihydroxyethylene urea;
- (j) multifunctional isocyanates, such as toluene diisocyanate, isophorone diisocyanate, methylene diisocyanate, xylene diisocyanate, and hexamethylene diisocyanate; and
- (k) other crosslinking agents for basic 15 water-absorbing resins known to persons skilled in the art.

A preferred surface crosslinking agent is a dihaloalkane, ethylene glycol diglycidyl ether (EGDGE), or a mixture thereof, which crosslink a basic resin at a temperature of about 25°C to about 150°C. Especially preferred surface crosslinking agents are dibromoalkanes containing 3 to 10 carbon atoms and EGDGE.

resins, or multicomponent SAP particles having an acidic resin on the exterior surface of the particles, suitable surface crosslinking agents are capable of reacting with acid moieties and crosslinking the acidic resin. Preferably, the surface crosslinking ing agent is alcohol soluble or water soluble, and possesses sufficient reactivity with an acidic resin such that crosslinking occurs in a controlled fash-

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ion, preferably at a temperature of about 25°C to about 150°C.

Nonlimiting examples of suitable surface crosslinking agents for acidic resins include:

- 5 (a) polyhydroxy compounds, such as glycols and glycerol;
 - (b) metal salts;

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- (c) quaternary ammonium compounds;
- (d) a multifunctional epoxy compound;
- (e) an alkylene carbonate, such as ethylene carbonate or propylene carbonate;
 - (f) a polyaziridine, such as 2,2bishydroxymethyl butanol tris[3-(1-aziridine propionate]);
 - (g) a haloepoxy, such as epichlorhydrin;
 - (h) a polyamine, such as ethylenediamine;
 - (i) a polyisocyanate, such as 2,4-toluene diisocyanate; and
- (j) other crosslinking agents for acidic 20 water-absorbing resins known to persons skilled in the art.

In addition to, or in lieu of, surface treating, the acidic resin, the basic resin, the matrix resin, or the entire SAP particle, or any combination thereof, can be annealed to improve water absorption and retention properties under a load. It has been found that heating a resin for a sufficient time at a sufficient temperature above the Tg (glass transition temperature) of the resin or microdomains improves the absorption properties of the resin. FIGS. 6 and 7 contain graphs showing the effect of annealing time and temperature on the absorption

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properties of a multicomponent SAP particle of the present invention comprising 55% by weight poly(vinylamine) and 45% by weight poly(acrylic acid), made by the method set forth hereafter in Example 12.

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The graphs in FIGS. 6 and 7 show that heating an SAP particle of the present invention for about 20 to about 120 minutes at a temperature of about 60°C to about 150°C improves absorption properties. The absorption properties, i.e., AUL and AUNL, graphed in FIGS. 6 and 7 are discussed in detail hereafter. Preferably, annealing is performed for about 30 to about 100 minutes at about 80°C to about 140°C. To achieve the full advantage of annealing, the SAP particles are annealed for about 40 to about 90 minutes at about 100°C to about 140°C.

In accordance with an important feature of the present invention, a strong acidic resin can be used with either a strong basic resin or a weak basic resin, or a mixture thereof. A weak acidic resin can be used with a strong basic resin or a weak basic resin, or a mixture thereof. Preferably, the acidic resin is a weak acidic resin and the basic resin is a weak basic resin. This result is unexpected in view of the ion exchange art wherein a combination of a weak acidic resin and a weak basic resin does not perform as well as other combinations, e.g., a strong acidic resin and a strong basic resin. In more preferred embodiments, the weak acidic resin, the weak basic resin, and/or the multicomponent SAP particles are surface crosslinked and/or annealed.

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As previously discussed, sodium poly(acrylate) conventionally is considered the best SAP, and, therefore, is the most widely used SAP in commercial applications. Sodium poly(acrylate) has polyelectrolytic properties that are responsible for its superior performance in absorbent applications. These properties include a high charge density, and charge relatively close to the polymer backbone.

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However, an acidic resin in the free acid form, or a basic resin in the free base form, 10 typically do not function as a commercially useful SAP because there is no ionic charge on either type of polymer. A poly(acrylic acid) resin, or a poly(vinylamine) resin, are neutral polymers, and, accordingly, do not possess the polyelectrolytic 15 properties necessary to provide SAPs useful commercially in diapers, catamenial devices, and similar absorbent articles. The driving force for water absorption and retention, therefore, is lacking. This is illustrated in Tables 1 and 2 showing 20 the relatively poor absorption and retention properties for a neutral poly(DAEA) in absorbing synthetic urine. However, when converted to a salt, an acidic resin, such as a polyacrylic acid, or a basic resin, such as a poly(dialkylaminoalkyl (meth)acrylamide), 25 then behave such as a commercially useful SAP.

It has been found that basic resins, in their free base form, are useful components in superabsorbent materials further containing an acidic water-absorbing resin. For example, a superabsorbent material comprising an admixture of a poly(dialkylaminoalkyl (meth)acrylamide) and an

acidic water-absorbing resin, such as polyacrylic acid, demonstrates good water absorption and retention properties. Such an SAP material comprises two uncharged, slightly crosslinked polymers, each of which is capable of swelling and absorbing aqueous media. When contacted with water or an aqueous electrolyte-containing medium, the two uncharged polymers neutralize each other to form a super-This also reduces the electroabsorbent material. lyte content of the medium absorbed by polymer, further enhancing the polyelectrolyte effect. Neither polymer in its uncharged form behaves as an SAP by itself when contacted with water. However, superabsorbent materials, which contain a simple mixture of two resins, one acidic and one basic, are capable of acting as an absorbent material because the two resins are converted to their polyelectrolyte form. These superabsorbent materials have demonstrated good water absorption and retention properties. However, the present multicomponent SAP particles, containing at least one microdomain of an acidic resin and at least one microdomain of a basic resin, exhibit improved water absorption and retention, and improved permeability, over simple mixtures of acidic resin particles and basic resin particles. 25

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In the present multicomponent SAP particles, the weak basic resin is present in its free base, e.g., amine, form, and the acidic resin is present in its free acid form. It is envisioned that a low percentage, i.e., about 25% or less, of the amine and/or acid functionalities can be in their charged form. The low percentage of charged

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functionalities does not adversely affect performance of the SAP particles, and can assist in the initial absorption of a liquid. A strong basic resin is present in the hydroxide or bicarbonate, i.e., charged, form.

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The present multicomponent SAP particles are useful in articles designed to absorb large amounts of liquids, especially electrolyte-containing liquids, such as in diapers and catamenial devices.

The following nonlimiting examples illustrate the preparation of the multicomponent SAP particles of the present invention.

EXAMPLE 1

Preparation of Poly(acrylic acid) 0% Neutralized (Poly(AA) DN=0)

A monomer mixture containing acrylic acid (270 grams), deionized water (810 grams), methylene-bisacrylamide (0.4 grams), sodium persulfate (0.547 grams), and 2-hydroxy-2-methyl-1-phenyl-propan-1-one (0.157 grams) was prepared, then sparged with nitrogen for 15 minutes. The monomer mixture was placed into a shallow glass dish, then the monomer mixture was polymerized under 15 mW/cm² of UV light for 25 minutes. The resulting poly(AA) was a rubbery gel.

The rubbery poly(AA) gel was cut into small pieces, then extruded through a KitchenAid Model K5SS mixer with meat grinder attachment. The extruded gel was dried in a forced-air oven at 120°C, and finally ground and sized through sieves to obtain the desired particle size.

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This procedure provided a lightly cross-linked polyacrylic acid hydrogel with a degree of neutralization of zero (DN=0).

EXAMPLE 2

Preparation of Poly(dimethylaminoethyl acrylamide) (Poly (DAEA))

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A monomer mixture containing 125 grams N-(2-dimethylaminoethyl) acrylamide (DAEA), 300 grams deionized water, 0.6 gram methylenebisacrylamide, and 0.11 grams V-50 initiator (i.e., 2,2'-azobis(2-ami-10 dinopropane) hydrochloride initiator available from Wako Pure Chemical Industries, Inc., Osaka, Japan) was sparged with argon for 15 minutes. Then the resulting reaction mixture was placed in a shallow dish and polymerized under 15 mW/cm² of UV light for 15 25 minutes. The polymerization was exothermic, eventually reaching about 100°C. The resulting lightly crosslinked poly(DAEA) was a rubbery gel. The rubbery poly(DAEA) gel was crumbled by hand, then dried at 60°C for 16 hours, and finally ground and 20 sized through sieves to obtain the desired particle size.

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EXAMPLE 3

Preparation of Poly(dimethylaminopropyl methacrylamide) (Poly(DMAPMA))

A monomer mixture containing DMAPMA monomer (100 grams), deionized water (150 grams), methylene-bisacrylamide (0.76 grams) and V-50 initiator (0.72 grams) was placed in a glass beaker. The monomer mixture was purged with argon for 25 minutes, covered, and then placed in an oven at about 60°C for about 60 hours. The resulting lightly crosslinked poly(DMAPMA) was a rubbery gel. The rubbery poly-(DMAPMA) gel was crumbled by hand, dried at 60°C for 16 hours, and then ground and sized through sieves to obtain the desired particle size.

15 EXAMPLE 4

Preparation of a Poly(N-vinylformamide) and a Poly(vinylamine)

A monomer mixture containing N-vinylform-amide (250 grams), deionized water (250 grams),

methylenebisacrylamide (1.09) grams), and V-50
initiator (0.42 grams) was placed in a shallow dish,
then polymerized under an ultraviolet lamp as set
forth in Example 1 until the mixture polymerized into
a rubbery gel. The lightly crosslinked poly(N-vinylformamide) then was hydrolyzed with a sodium hydroxide solution to yield a lightly crosslinked poly(vinylamine).

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EXAMPLE 5

Preparation of a Strong Acidic Water-Absorbing Resin

A monomer mixture containing acrylic acid

(51 grams), 2-acrylamido-2-methyl-1-propanesulfonic
acid (AMPS, 25.8 grams), deionized water (230 grams),
methylenebisacrylamide (0.088 grams), sodium persulfate (0.12 grams), and 2-hydroxy-2-methyl-1-phenylpropan-1-one (0.034 grams) was prepared, then placed
in shallow dish and polymerized under an ultraviolet
lamp as set forth in Example 1 until the monomer
mixture polymerizes into rubbery gel.

The gel was cut into small pieces then extruded through a KitchenAid Model K5SS mixer with a meat grinder attachment. The extruded gel then was dried in a forced-air oven at 120°C, ground, and sized through sieves to obtain the desired particle size.

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This resulting lightly crosslinked acidic resin contained 15 mole percent strong acid functionality (-SO₃H) and 85 mole percent weak acid functionality (-CO₂H).

EXAMPLE 6

Preparation of a Crosslinked Poly(vinyl alcohol-co-vinylamine) Resin

Poly(vinyl alcohol-co-vinylamine) (50 grams, 6 mol% vinylamine), available from Air Products Inc., Allentown, PA, was dissolved in 450 grams of deionized water in a glass jar to form a viscous

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solution. Ethylene glycol diglycidyl ether (0.2 grams) was added to the viscous solution, with stirring. The jar then was covered and placed in a 60°C oven for 16 hours to yield a rubbery gel of a lightly crosslinked poly(vinyl alcohol-co-vinylamine).

EXAMPLE 7

Preparation of a Crosslinked Poly(vinylamine) Resin

poly(vinylamine) solution was added 0.18 g of ethyleneglycol diglycidyl ether (EGDGE). The resulting mixture was stirred to dissolve the EGDGE, then the mixture was heated to about 60°C and held for one hour to gel. The gel was heated to about 80°C and held until about 90% of the water was removed. The resulting get then was extruded and dried to a constant weight at 80°C. The dried, lightly crosslinked poly(vinylamine) then was cryogenically milled to form a granular material.

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EXAMPLE 8

Preparation of a Poly(DAEA)/Poly(AA) Multicomponent SAP (Poly(AA) Continuous Phase)

The undried, rubbery poly(AA) hydrogel prepared in Example 1 (133 grams) was cut into pieces and extruded through a KitchenAid Model K5SS mixer with meat grinder attachment. The gel then was mixed with 50 grams of the dry poly(DAEA) particles (<106 microns in size) prepared in Example 2. The result-

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ing mixture was extruded three times using the KitchenAid mixer, then dried in a 60°C forced-air oven for 16 hours and finally ground and sized through sieves to obtain the desired particle size. The process yielded 83 grams of multicomponent SAP particles comprising poly(DAEA) microdomains dispersed in a continuous poly(AA) phase, and having a weight ratio of poly(DAEA) to poly(AA) of about 60/40.

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EXAMPLE 9

Surface Treatment of the Poly(DAEA)/ Poly(AA) Multicomponent SAP of Example 8

A surface-treating solution was prepared by admixing 0.15 grams EGDGE, 7.88 grams propylene glycol, and 1.97 grams deionized water until homoge-15 neous. Ten grams of the poly(DAEA)/poly(AA) multicomponent SAP of Example 8 were placed in a beaker fitted with a vertical shaft stirrer. The dry multicomponent SAP was stirred at a sufficient speed to fluidize the SAP in the beaker, then 0.4 grams of the 20 surface-treating solution was added to the fluidized SAP dropwise via syringe. Then, stirring was stopped, and the beaker was placed in a 125°C forcedair oven for one hour to yield a poly(DAEA)/poly(AA) multicomponent SAP surface treated with 600 ppm of 25 EGDGE.

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EXAMPLE 10

Preparation of a Poly(AA)/Poly(DMAPMA) Multicomponent SAP (Poly(DMAPMA) Continuous Phase)

The poly(DMAPMA) hydrogel prepared in Example 3 (70 grams) was cut into pieces and extruded 5 through a KitchenAid Model K5SS mixer with meat grinder attachment. The gel then was mixed with 32 grams of dry poly(AA) particles (<106 microns in size) prepared in Example 1. The resulting mixture then was extruded three times using the KitchenAid 10 mixer, followed by drying in a 60°C forced-air oven at 60°C for 16 hours, and finally grinding and sizing through sieves to obtain the desired particle size. The process yielded 60 grams of multicomponent SAP particles comprising poly(AA) microdomains dispersed 15 in a continuous poly(DMAPMA) phase, and having a poly(AA) to poly(DMAPMA) weight ratio of about 50/50.

EXAMPLE 11

Surface Treatment of the Poly(AA)/ 20 Poly(DMAPMA) Multicomponent SAP of Example 10

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A surface-treating solution was prepared by admixing 0.375 grams 1,8-dibromooctane and 9.625 grams isopropanol until homogeneous. Ten grams of the poly(AA)/poly(DMAPMA) multicomponent SAP of Example 10 were placed in a beaker fitted with a vertical shaft stirrer. The dry multicomponent SAP was stirred at a sufficient speed to fluidize the SAP in the beaker, then 0.4 grams of the surface-treating solution was added to the fluidized SAP dropwise via

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syringe. Next, stirring was stopped, and the beaker was placed in a 105°C forced-air oven for one hour to yield a poly(AA)/poly(DMAPMA) multicomponent SAP surface treated with 1,500 ppm of 1,8-dibromooctane.

EXAMPLE 12

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Poly(DAEA)/Poly(AA) Multicomponent SAP Prepared by Gel Coextrusion

were extruded through a KitchenAid Model K5SS mixer with meat grinder attachment. Twenty-four grams of the poly(AA) hydrogel of Example 1 also were extruded through a KitchenAid Model K5SS mixer with meat grinder attachment. The two extrudates then were combined via hand mixing, followed by extruding the resulting mixture two times using the meat grinder. The extruded product then was dried for 16 hours at 60°C, milled and sized to 180-710 microns, and finally surface treated with 200 ppm EGDGE (as described in Example 9). The procedure yields multicomponent SAP containing microdomains of poly(DAEA) and poly(AA), and having poly(DAEA)/poly(AA) weight ratio of about 60/40.

EXAMPLE 13

Preparation of Poly(vinylquanadine) (Poly(VG))

To 500 ml of an aqueous solution of poly-(vinylamine) (1.98% solids, 93% hydrolyzed) was added 38.5 ml of 6M hydrochloric acid and 9.65g of cyanamide (H_2NCN). The resulting solution was heated

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under reflux for 8 hours. The solution next was diluted to a volume of 3L (liters) with a 5% sodium hydroxide solution, then ultrafiltered (M, cut off of 100,000) with 15L of a 5% sodium hydroxide solution, followed by 15L of deionized water. The resulting 5 product was concentrated to a 2.6% solids solution, having a pH 11.54. A poly(vinylamine) solution has a pH 10.0. The 2.6% solids solution gave a negative silver nitrate test, and a gravimetric analysis of the polymer, after the addition of HCl, gave the 10 following composition: vinylguanidine 90%, vinylformamide 7%, and vinylamine 3%. Infrared analysis shows a strong absorption at 1651 cm⁻¹, which is not present in poly(vinylamine), and corresponds to a C=N stretch. 15

EXAMPLE 14

Preparation of a Crosslinked Poly(VG) Resin

The 2.6% solids solution of Example 13 was further concentrated to 12.5% solids by distillation.

To this 12.5% solids solution was added 1 mole % EGDGE, and the resulting solution then was heated in a 60°C oven for 5 hours to form a gel of lightly crosslinked poly(vinylguanidine).

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EXAMPLE 15

Preparation of a Coextruded Poly(VG)/Poly(AA) Multicomponent SAP

The crosslinked poly(VG) hydrogel of Exam
5 ple 14 was coextruded with 1 mole equivalent of the poly(AA) of Example 1 by the method set forth in Example 12. A portion of the coextruded poly(VG)/-poly(AA) multicomponent SAP then was surface crosslinked with 200 ppm EGDGE, by the method set forth in Example 9.

EXAMPLE 16

PEI/Poly(AA) Coextruded Multicomponent SAP Prepared by Gel Coextrusion

Aqueous solutions containing 10% and 20% by weight polyethylenimine (PEI, M, of 60,000, available 15 commercially as EPOMIN P-1000, Aceto Corp., Lake Success, NY) were crosslinked with 1.0 and 1.5 mole % EGDGE by the method set forth in Example 6, i.e., heating for 16 hours at 60°C, to provide rubbery gels. The rubbery PEI gels (37.4 wt.%) were coex-20 truded with the poly(AA) gel of Example 1 (62.6 wt.%) in accordance with the method set forth in Example 12, and the resulting coextruded multicomponent SAPs were dried in an oven at 60°C. The dried multicomponent SAPs were cryogenically milled, and then 25 sized.

In the test results set forth below, the multicomponent SAP particles of the present invention

were tested for absorption under no load (AUNL) and absorption under load at 0.28 psi and 0.7 psi (AUL (0.28 psi) and AUL (0.7 psi)). Absorption under load (AUL) is a measure of the ability of an SAP to absorb fluid under an applied pressure. The AUL was determined by the following method, as disclosed in U.S. Patent No. 5,149,335, incorporated herein by reference.

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An SAP (0.160 g +/-0.001 g) is carefully scattered onto a 140-micron, water-permeable mesh 10 attached to the base of a hollow Plexiglas cylinder with an internal diameter of 25mm. The sample is covered with a 100 g cover plate and the cylinder assembly weighed. This gives an applied pressure of 20 g/cm^2 (0.28 psi). Alternatively, the sample can 15 be covered with a 250 g cover plate to give an applied pressure of 51 g/cm^2 (0.7 psi). The screened base of the cylinder is placed in a 100mm petri dish containing 25 milliliters of a test solution (usually 0.9% saline), and the polymer is allowed to absorb 20 for 1 hour (or 3 hours). By reweighing the cylinder assembly, the AUL (at a given pressure) is calculated by dividing the weight of liquid absorbed by the dry weight of polymer before liquid contact.

The following tables contain absorption and retention data for the multicomponent SAP particles of the present invention, for individual polymers present in the multicomponent SAP particles, and for simple admixtures of the dry resins present in the multicomponent SAP particles. The data shows a significant improvement in water absorption and retention for the present multicomponent SAP parti-

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cles containing microdomains of an acidic and/or basic resin polymers within each particle compared to the individual resins and a simple admixture of the individual resins. The data in Tables 1-6 shows the improved ability of multicomponent SAP particles of the present invention to absorb and retain an aqueous 0.9% saline solution.

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		Table	e 1			
SAP	AUL (0.28 psi, 1 hr.)	AUL (0.7 psi, 1 hr.)	AUNL (1 hr.)	AUL (0.28 psi, 3 hr.)	AUL (0.7 psi, 3 hr.)	AUNI (3 hr.)
Poly(DAEA) alone1)	9.6	8.1	23.9	13.5	9.3	24.2
Polyacrylic Acid alone?	11.9	10.8	14.3	12.0	10.8	14.3
SAP-131	11.0	10.9	45.2	14.8	14.4	48.0
SAP-241	12.5	9.6	26.7	18.9	13.1	30.1
SAP-351	12.4	11.3	37.3	16.5	14.7	42.3
SAP-461	20.1	17.2	28.6	24.7	20.7	34.1
SAP-571	25.3	18.2	35.3	28.1	23	38.7
Multicomponent SAP-181						
0,60	23.7	16.3	41.6	26.9	20	41.7
200	26.7	24.7	41.2	27.1	25.1	39.9
400	27.3	24.1	43.4	27.5	24.5	44.0
600	29.2	23.8	41.8	29.5	24.0	41.2
800	26.6	24.1	40.9	26.7	24.2	41.7
1,000	27.5	24.3	39.9	27.8	24.2	40.7

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		Table 1	e 1			
SAP	AUL (0.28 psi, 1 hr.)	AUL (0.7 psi, 1 hr.)	AUNL (1 hr.)	AUL (0.28 psi, 3 hr.)	AUL (0.7 psi, 3 hr.)	AUNL (3 hr.)
Multicomponent SAP-2101						
160	26.3	15.4	40	26.9	17.3	39.4
400	26.5	20.5	39.3	27	22.4	40.3
009	27	18.3	40.2	27.1	20.7	40.6

particle size--180-710 µm;

08 neutralization, particle size--180-710 µm, surface crosslinked--600 ppm EGDGE;

mixture of 60% poly(DAEA), particle sizes less than 180 nm, and 40% polyacrylic acid --0% neutralized; Ē

and 40% polyacrylic acid --0% neutralized, " mixture of 60% poly(DAEA), particle sizes less than 180 nm, crosslinked with 600 ppm EGDGE;

mixture of 60% poly(DAEA), particle size--180-710 µm, and 40% polyacrylic acid --0% neutralized;

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60% poly(DAEA), particle size--180-710 µm, and 40% polyacrylic acid --0% neutralized, crosslinked with 600 ppm EGDGE; " mixture of

" mixture of 60% poly(DAEA), particle sizes less than 180 µm, and 40% polyacrylic acid--20% neutralized, particle size 180-710 µm;

multicomponent SAP containing microdomains of poly(DAEA) (<180 µm) as dispersed phase in poly(AA) (DN=0) continuous phase, poly(DAEA)/poly(AA) weight ratio--60/40;

ppm surface crosslinking with EGDGE; and

multicomponent SAP containing microdomains of poly(DAEA) (<180 µm) as dispersed phase in poly(AA) (DN=20) continuous phase, poly(DAEA)/poly(AA) weight ratio--60/40. <u>ē</u>

		Table 2	2			
SAP	AUL (0.28 psi, 1 hr.)	AUL (0.7 psi, 1 hr.)	AUNL (1 hr.)	AUL (0.28 psi, 3 hr.)	AUL (0.7 psi, 3 hr.)	AUNL (3 hr.)
Poly (DMAPMA) ¹¹¹	10.2	8.6	18	11.4	10	18.3
Poly (DMAPMA) ¹²⁾	9.3	5.2	17.4	11	6.9	17.8
Polyacrylic acid ¹³⁾	11.9	10.8	14.3	12.0	10.8	14.3
SAP-614)	14.5	10.9	18.8	17.2	14.3	20.9
SAP-7181	14	12	38.7	17.9	15.7	43.6
SAP-8161	12.5	10.4	24.8	14.5	12.4	24.8
Multicomponent SAP-317)						
(60	28.8	15	41.6	31	17.5	41.5
100	27.4	24.2	38.8	27.1	23.6	38.8
200	27.3	24.2	39.8	25.8	23	39
400	26	23	37	25.2	22.5	36.4
009	25.1	22.3	37.1	24.7	21.3	36.1
Multicomponent SAP-4 ¹⁸¹						
0,81	31.9	11.6	44.2	31.8	15.7	44.9
200	27.6	24.3	37.8	27.5	23.4	38.1
400	27.5	23.7	37.4	27.2	23.1	38.8

		Table 2	2			
SAP	AUL (0.28 ps1, 1 hr.)	AUL (0.7 psi, 1 hr.)	AUNL (1 hr.)	AUL (0.28 psi, 3 hr.)	AUL (0.7 psi, 3 hr.)	AUNL (3 hr.)
Multicomponent SAP-5191						
0201	23.6	12.9	37.9	25	14.4	38.5
1500	24.7	16.9	36.4	25.5	18.3	37.5

Poly(DMAPMA), particle size less than 106 µm;

Poly(DMAPMA), particle size 106-180 µm;

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Polyacrylic acid, particle size 180-710 µm--08 neutralized, surface crosslinked with 600 ppm BGDGE;

mixture of 60% Poly(DMAPMA), particle size 106-180 µm, and 40% polyacrylic acid--0% neutralized; Î

mixture of 60% Poly(DMAPMA), particle size <106 µm, and 40% polyacrylic acid--0% neutralized; 2

16 mixture of 50% Poly(DMAPMA), and 50% polyacrylic acid--0% neutralized;

17) multicomponent SAP containing microdomains of poly(DMAPMA) (<106µm) as dispersed phase in poly(AA) (DN=0) continuous phase, poly(DMAPMA)/poly(AA) weight ratio 60/40;

10) multicomponent SAP containing microdomains of poly(DMAPMA) (106-180 µm) as dispersed phase in poly(AA) (DN=0) continuous phase, poly(DMAPMA)/poly(AA) weight ratio 60/40;

19) multicomponent SAP containing microdomains of poly(AA) (DN=0%) (<106 µm) as dispersed phase in poly(DMAPMA) continuous phase, poly(AA)/poly(DMAPMA) weight ratio 50/50; and

20) ppm surface crosslinking with dibromooctane.

		Table 3	3			
				AUL (0.28	AUL (0.7	
SAP	AUL (0.28 psi, 1 hr.)	AUL (0.7 psi, (1 hr.)	AUNL (1 hr.)	psi, 3 hr.)	pst, 3 hr.}	AUNL (3 hr.)
	14.2	14.4	21.4	15	14.3	23.4
Poly(vinylamine) alone	7.1.		28.2	23.8	20.5	36.3
SAP-9211	21.2	18.0	2.07			
Milticomponent SAP-6221						
and dispersion of the second	6	12.8	53.8	16.9	15.6	55.4
0	6.11			3 7.6	30.1	45.5
100	37.5	30.1	45.3	5:,5		
000	2.91	30.4	48.5	35.9	30.2	47.4
002	2.40	9 05	44.9	34.6	30.6	46.2
400	34.0	2.25				

mixture of 37% poly(vinylamine) and 63% poly(AA); and

22) multicomponent SAP containing microdomains of poly(vinylamine) (<180 µm) as dispersed phase in poly(AA) (DN=0) continuous phase, poly(vinylamine)/poly(AA) weight ratio--37/63.

		AUNL (3 hr.)	40.2	39.9
		AUL (0.7 psi, 3 hr.)	16.3	27.3
	Example 12 poly(AA)	AUL (0.28 psi, 3 hr.)	30.6	30.8
Table 4	oextruded Multicomponent SAP of Example (60/40 weight ratio poly(DAEA)/poly(AA))	AUNL (1 hr.)	41.1	40.2
	Coextruded Multicomponent SAP of Example 12 (60/40 weight ratio poly(DAEA)/poly(AA))	AUL (0.7 psi, 1 hr.)	13.3	7.72
		AUL (0.28 psi, 1 hr.)	30.5	31
		Surface Treatment	0	200 ppm EGDGE

		Table 5	5			
SAP	AUL (0.28 psi, 1 hr.)	AUL (0.7 psi, 1 hr.)	AUNL (1 hr.)	AUL (0.28 psi, 3 hr.)	AUL (0.7 psi, 3 hr.)	AUNL (3 hr.)
Poly(vinylguanidine) hydro- chloride alone	21	16.1	31.2	22.4	18.0	32.7
Multicomponent SAP-723						
(60	18.8	12.7	40.6	21.2	15.3	46.8
200	22	19.2	33.5	23.5	20.3	37.4

 $^{23)}$ multicomponent SAP containing microdomains of poly(VG) and poly(AA), with a poly(VG)/poly(AA) weight ratio--50/50.

				_	
			AUNI (3	34.9	31.9
		AUL (0.7	psi,	20.8	18.1
	Example 16 ly(AA))	AUL (0.28	psi,	24.3	22.4
Table 6	nent SAP of ratio PEI/po	,	AUNL (1	32	28.4
Та	Coextruded Multicomponent SAP of Example 16 (37.4/62.6 weight ratio PEI/poly(AA))	AUL (0.7	psi,	19.5	16.2
	Coextrude (37.4/	AUL (0.28	psi,	23	20.1
		Cross-	linker	1.0	1.5
		PEI Gel	(% Sol-	20	10

" mole % EGDGE.

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EXAMPLE 17

Preparation of a Multicomponent SAP Having a Poly(AA) Core Surrounded by a PEI Shell

Sorbitan monooleate (0.81 g) was dissolved in 200 ml of heptane. Ten grams of crosslinked, unneutralized polyacrylic acid (180-425 μ m) was added to this solution to act as seed for the core/shell composite particles. The resulting mixture was stirred at 700 rpm with a paddle stirrer. Polyethyleneimine (PEI) (27.6 g, 30% in water, 10 M_=750,000) was added to the polyacrylic acid/heptane slurry, followed immediately by the addition of 3.6 g of EGDGE. The EGDGE and PEI were allowed to cure for 4.5 hours at room temperature. The resulting SAP particles were allowed to settle, and the super-15 natant heptane was decanted. The SAP particles were rinsed three times with 100 ml of acetone. particles were allowed to dry overnight at room temperature, then further dried at 80°C for 2 hours to yield 23.43 g of the multicomponent SAP parti-20 cles.

The SAP particles of Example 17 then were tested for an ability to absorb synthetic urine under no load (AUNL) and under load (AUL) at 0.28 psi and 0.7 psi, in accordance with the previously described method. The results are summarized below:

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Surface Treatment	AUNL (1 hr)	AUL 0.28 psi (1 hr)	AUL 0.7 psi (1 hr)	AUNL (3 hr)	AUL 0.28 psi (3 hr)	AUL 0.7 psi (3 hr)
None	15.22	12.09	10.38	15.78	13.12	11.74

EXAMPLE 18

Preparation of a Multicomponent SAP Having a Poly(AA) Core Surrounded by a Poly(vinylamine) Shell

Sorbitan monooleate (1.88 g) was dissolved in 500 ml of heptane. Ten grams of crosslinked, unneutralized polyacrylic acid (180-425 μ m) was added to this solution to act as seed for the core/shell composite particles. The resulting mixture was stirred at 700 rpm with a paddle stirrer. Poly(vinylamine) (84 g, 10.67% in water, M_>100,000) was added to the polyacrylic acid/heptane slurry, followed immediately by the addition of 1.5 g of EGDGE. The EGDGE and poly(vinylamine) were allowed to cure for 6 hours at room temperature. The resulting SAP particles were allowed to settle, and the supernatant heptane was decanted. The SAP particles were rinsed three times with 200 ml of acetone. The SAP particles were dried at 80°C for 3 hours to yield 17.89 g of the multicomponent SAP particles.

The SAP particles of Example 18 then were tested for an ability to absorb synthetic urine.

The results are summarized below:

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Surface Treatment	AUNL (1 hr)	AUL 0.28 psi (1 hr)	AUL 0.7 psi (1 hr)	AUNL (3 hr)	AUL 0.28 psi (3 hr)	AUL 0.7 psi (3 hr)
None	49.88	39.28	33.20	51.83	41.79	35.23

EXAMPLE 19

5 Preparation of a Multicomponent SAP Containing Agglomerated Poly(AA)

and Poly(vinylamine)

An agglomeration solution containing the following ingredients was prepared:

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2.5 hours.

0.25 g EGDGE

0.32 g Aluminum sulfate

0.31 g Magnesium sulfate

4.10 g Water

15.0 g Propylene glycol.

- 15 Under rapid agitation, 2.1 g of poly(vinylamine)
 (<180 μm, 5 mole % crosslinked with EGDGE) and 2.38
 g of poly(AA) (<180 μm, 0.07 mole % crosslinked with
 MBA) were fluidized. With continued mixing, 0.84 g
 of the agglomeration solution was added to the
 20 fluidized powder blend. The resulting SAP particles
 were spread on a glass dish and dried at 125°C for
 - The ability of the SAP particles to absorb and retain synthetic urine was determined. The results are summarized below:

Surface Treatment	AUNL (1 hr)	AUL 0.28 psi (1 hr)	AUL 0.7 psi (1 hr)	AUNL (3 ḥr)	AUL 0.28 psi (3 hr)	AUL 0.7 psi (3 hr)
None	55.09	40.40	31.22	56.71	41.01	37.80

EXAMPLE 20

5 Preparation of a Multicomponent SAP
Comprising an Interpenetrating Polymer
Network of Poly(AA) and Poly(vinylamine)

Reticulated poly(sodium acrylate) polymer beads (1.19 g) were acidified with 20 ml of 1M HCl, and allowed to stand for 1.5 hours. The poly(AA) 10 beads then were filtered on a medium glass frit and rinsed with 50 ml of isopropyl alcohol. Air was drawn through the acidified poly(AA) beads for 0.5 hour to remove isopropyl alcohol from the pores of the poly(AA). The poly(AA) foam beads then were 15 added to a premixed solution of 11.0 g of poly-(vinylamine) (10.67%, M2>100,000) and 0.24 g of The resulting mixture coagulated and was allowed to cure for 2 hours at 60°C. The resulting 20 multicomponent SAP particles were spread on a dish and dried at 60°C overnight to yield 2.8 g of the agglomerated SAP particles. A portion of the resulting multicomponent SAP particles was annealed at 125°C for 1 hour to effect surface crosslinking. 25 The remaining portion of the particles was not annealed. The ability of the IPN SAP particles of Example 20 were tested for an ability to absorb and retain synthetic urine. The results are summarized below:

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Surface Treatment	AUNL (1 hr)	AUL 0.28 psi (1 hr)	AUL 0.7 psi (1 hr)	AUNL (3 hr)	AUL 0.28 psi (3 hr)	AUL 0.7 psi (3 hr)
None			22.1			22.4
Annealing for 1 hr @ 125°C	32.8	25.2	21.7	34.	22.9	22.8

EXAMPLE 21

Preparation of a Multicomponent SAP
Comprising a Layer of Poly(AA) in Laminar
Contact with a Layer of Poly(vinylamine)

To 186 g of 5 wt% poly(AA) (M, of about 1.25×10^6) in water was added 1.18 g of EGDGE, and the viscous solution was mixed thoroughly. Separately, 106 g of poly(vinylamine) (10.67%, M_>100,000) and 2.3 g of EGDGE were quickly mixed and 15 spread on a 9" x 13" Teflon-coated metal sheet, then cured at 80°C for 10 minutes. Next, the poly(AA) solution was spread on the poly(vinylamine) gel and allowed to cure and dry at 80°C for 4 hours. The sheets shrunk during drying, and then the laminate 20 was comminuted. A portion of the resulting multicomponent SAP particles was neither surface crosslinked nor annealed. A second portion was annealed at 125°C for 1 hour. A third portion was surface crosslinked with PG/H₂O at 120°C in an iden-25 tical manner as Example 19. The SAP particles of Example 21 were tested for an ability to absorb and retain synthetic urine. The results are summarized below:

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Surface Treatment	AUNL (1 hr)	AUL 0.28 psi (1 hr)	AUL 0.7 psi (1 hr)	AUNL (3 hr)	AUL 0.28 psi (3 hr)	AUL 0.7 psi (3 hr)
None	32.4	22.4	23.7	35.1	25.1	27
Annealed for 1 hr @ 125°C	25.3	20.1	22.1	29.1	21.7	24.4
Cross- linked with PG/H ₂ O (80/20)	27	20.5	20.8	29.7	22.3	24.7

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particle of the present invention can contain an acidic resin and/or a basic resin that is partially neutralized, a series of tests was performed on multicomponent SAP particles containing 45% by weight poly(AA) and 55% by weight poly(vinylamine). The multicomponent SAP particles were prepared as set forth in Example 12, but the percent neutralization of the poly(AA) and poly(vinylamine) was changed. The various multicomponent SAP particles were tested for an ability to absorb and retain synthetic urine, and the results are summarized in Table 7.

		Table 7		
5	<pre>% Neutralized Poly(vinylamine)/ % Neutralized Poly(AA) (by weight)</pre>	Surface Crosslinking	AUL (0.7 psi, 1 hr)	AUL (0.7 psi, 3 hr)
	0/0	None	16.8	21.6
	0/10	None	13.4	16.9
	0/25	None	12.6	16
	10/0	None	37.2	37.7
10	25/0	None	24.4	25.3
	10/10	None	19.2	24.3
	25/25	None	19.8	19.3
	50/50	None	11.9	13.8
	0/0	PG/H ₂ O ²⁵¹	43.3	47.6
15	0/10	PG/H ₂ O	34	36.9
	0/25	PG/H ₂ O	14.4	17.4
	10/0	PG/H ₂ O	30.9	31.4
	25/0	PG/H ₂ O	24.1	25.3
	10/10	PG/H ₂ O	39.3	41.2
20	25/25	PG/H ₂ O	18.9	18.7
	50/50	PG/H;O	12.1	14.5

Surface treatment with propylene glycol/water (80/20 ratio) as set forth in Example 19.

In another series of tests, the ratio of
acidic water-absorbing resin to basic water-absorbing resin in the multicomponent SAP particles was
varied. In particular, Table 8 summarizes the AUNL
data and the AUL data at different pressures for a
series of multicomponent SAP particles containing
poly(vinylamine) and poly(AA) over the range of 25%
to 75% by weight. The multicomponent SAP particles
used in this series of tests were prepared in accor-

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dance with the multicomponent SAP particles prepared in Example 12, and contained 55% by weight poly(vinylamine) and 45% by weight poly(acrylic acid).

All multicomponent SAP particles used in the test were surface crosslinked with 50 ppm EGDGE. The multicomponent SAP particles were tested for an ability to absorb and retain synthetic urine.

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						Table 8						
Weight Ratio Poly(vinyl amine)/- Poly(AA)	AUL 0.28 psi (1 hr)	AUL 0.7 psi (1 hr)	AUL 1.4 psi (1 hr)	AUNL (1 hr)	AUL 0.28 psi (3 hr)	AUL 0.7 psi (3 hr)	AUL 1.4 psi (3 hr)	AUNL (3 hr)	AUL 0.28 psi (17 hr)	AUL 0.7 psi (17 hr)	AUL 1.4 psi (17 hr)	AUNL (17 hr)
25/75	41.3	36.6		53.6	41.2	36.6		54	39.1	33.3		52.3
30/70	46.3	42.2		58.7	46.4	42.8		59.6	43.1	38.7		58.4
35/65	43.6	38.5		54.4	44.2	39.5		54.8	42	35.8		54.3
40/60	52.1	. 44.3		63.9	53.7	46.5		66.7	51.7	43.2		65.2
45/55	50.4	46		61.1	51.4	47.4		63.2	47.3	41.9		61.9
50/50	52.2	45	26	62.5	54.8	47.7	29	66.7	52.8	45.4	30.9	66.4
55/45	52.1	47.3	27.4	62.5	54.8	49.3	31.3	66.2	53.1	44.8	32.5	65.4
60/40	52.8	47	27.8	64.6	55.2	49.6	30.9	89	52.6	44	33	9.79
65/35	50	45.9		59.2	51.6	47.3		61.8	48.8	41		61.4
70/30	47.5	43.1		57.4	48.3	43.8		59.4	43.5	37.2		56.7
75/25	43.9	39.3		53.6	43.9	39.2		54.8	38.9	31.2		51.4

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In another series of tests, multicomponent SAP particles containing 45% poly(AA) and 55% poly-(vinylamine) by weight were prepared as set forth in Example 12. The multicomponent SAP particles were prepared by extruding the blended gels of acidic resin 5 and basic resin using a KitchenAid mixer (as a control), or using a Brabender twin screw extruder containing both mixing and conveying elements. In some tests, additional back pressure was provided by a breaker plate and/or a screen. The speed of the 10 Brabender extruder was varied. Both untreated and surface treated (i.e., PG/H_2O 80/20) multicomponent SAP particles were tested. The various samples were tested for an ability to absorb synthetic urine. The results, summarized in Table 9, show that the more intimate 15 blending provided by the Brabender extruder improved the absorption and retention properties of the SAP particles.

	Table	e 9					
	Surface	AUNL	AUL 0.28 psi	AUL 0.7 psi	AUNL	AUL 0.28 psi	AUL 0.7 psi
Method of Extrusion	Treatment	(1 hr)	(1 hr)	(1 hr)	(3 hr)	(3 nr)	(3 1117)
KitchenAid (control)	None	9.69	33	15.4	73.3	39.3	21.7
Brabender-no plate 25 rpm	None	71.4	41.7	13.9	74.7	46.6	19.6
	None	7.07	43.5	15.5	73.8	56.2	23.6
Brabender-plate 25 rpm	None	72	46.7	16	74.1	55.1	22.1
100	None	70.5	48.4	16.9	72.6	09	23.2
Brabender-plate 150 rpm	None	69.7	50.5	29.5	72.1	59.3	35.4
Brabender-plate 40 mesh screen 25 rpm	None	70.5	54.4	16.3	73.3	59.7	23.9
Brabender-plate 40 mesh screen 150 rpm	None	68.9	57.7	33.2	69	59.9	42.1
witchenbid (control)	PG/H ₂ O 80/20	64.3	51.9	40.3	6.9	55.7	44
Rrahender-no plate 25 rpm	PG/H2O 80/20	66.2	53.7	42	70.4	56.9	44.6
plate 100	PG/H2O 80/20	65.4	52.8	41.6	68.8	56.1	45.4
ite 25 rpm	PG/H2O 80/20	66.8	53.7	42.3	70.4	56.9	45.5
	PG/H ₂ O 80/20	99	53	44	68.8	55.5	47.6
Brabender-plate 150 rpm	PG/H ₂ O 80/20	65.5	52.3	44.6	67.8	54.5	47.2
Brabender-plate 40 mesh screen 25 rpm	PG/H2O 80/20	65.2	54	45.6	68.3	56.2	49.1
Rrahender-plate 40 mesh screen 150 rpm	PG/H ₂ O 80/20	63.5	50.7	44.2	64.9	53.1	47.1

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In addition to an ability to absorb and retain relatively large amounts of a liquid, it also is important for an SAP to exhibit good permeability, and, therefore, rapidly absorb the liquid. Therefore, in addition to absorbent capacity, or gel 5 volume, useful SAP particles also have a high gel strength, i.e., the particles do not deform after absorbing a liquid. In addition, the permeability or flow conductivity of a hydrogel formed when SAP particles swell, or have already swelled, in the 10 presence of a liquid is extremely important property for practical use of the SAP particles. Differences in permeability or flow conductivity of the absorbent polymer can directly impact on the ability of an absorbent article to acquire and distribute body 15 fluids.

Many types of SAP particles exhibit gel blocking. "Gel blocking" occurs when the SAP particles are wetted and swell, which inhibits fluid transmission to the interior of the SAP particles 20 and between absorbent SAP particles. Wetting of the interior of the SAP particles or the absorbent structure as a whole, therefore, takes place via a very slow diffusion process, possibly requiring up to 16 hours for complete fluid absorption. In prac-25 tical terms, this means that acquisition of a fluid by the SAP particles, and, accordingly, the absorbent structure, such as a diaper, can be much slower than the rate at which fluids are discharged, especially in gush situations. Leakage from an absor-30 bent structure, therefore, can occur well before the SAP particles in the absorbent structure are fully

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saturated, or before the fluid can diffuse or wick past the "gel blocked" particles into the remainder of the absorbent structure. Gel blocking can be a particularly acute problem if the SAP particles lack adequate gel strength, and deform or spread under stress after the SAP particles swell with absorbed fluid.

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Accordingly, an SAP particle can have a satisfactory AUL value, but will have inadequate permeability or flow conductivity to be useful at high concentrations in absorbent structures. In order to have a high AUL value, it is only necessary that the hydrogel formed from the SAP particles has a minimal permeability such that, under a confining pressure of 0.3 psi, gel blocking does not occur to any significant degree. The degree of permeability needed to simply avoid gel blocking is much less than the permeability needed to provide good fluid transport properties. Accordingly, SAPs that avoid gel blocking and have a satisfactory AUL value can still be greatly deficient in these other fluid handling properties.

Accordingly, an important characteristic of the multicomponent SAP particles of the present invention is permeability when swollen with a liquid to form a hydrogel zone or layer, as defined by the Saline Flow Conductivity (SFC) value of the SAP particles. SFC measures the ability of an SAP to transport saline fluids, such as the ability of the hydrogel layer formed from the swollen SAP to transport body fluids. A material having relatively high SFC value is an air-laid web of woodpulp fibers.

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Typically, an air-laid web of pulp fibers (e.g., having a density of 0.15 g/cc) exhibits an SFC value of about 200 x 10^{-7} cm³sec/g. In contrast, typical hydrogel-forming SAPs exhibit SFC values of 1 x 10^{-7} cm³sec/g or less. When an SAP is present at high concentrations in an absorbent structure, and then swells to form a hydrogel under usage pressures, the boundaries of the hydrogel come into contact, and interstitial voids in this high SAP concentration region become generally bounded by hydrogel. When this occurs, the permeability or saline flow conductivity properties in this region is generally indicative of the permeability or saline flow conductivity properties of a hydrogel zone formed from the SAP alone. Increasing the permeability of these swollen high concentration regions to levels that approach or even exceed conventional acquisition/distribution materials, such as wood pulp fluff, can provide superior fluid handling properties for the absorbent structure, thus decreasing incidents of leakage, especially at high fluid loadings.

Accordingly, it would be highly desirable to provide SAP particles having an SFC value that approaches or exceeds the SFC value of an air-laid web of wood pulp fibers. This is particularly true if high, localized concentrations of SAP particles are to be effectively used in an absorbent structure. High SFC values also indicate an ability of the resultant hydrogel to absorb and retain body fluids under normal usage conditions.

The SFC value of the present multicomponent SAP particles are substantially improved over

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the SFC value for a standard poly(AA) SAP, as illustrated in the data summarized in Table 10. A method for determining the SFC value of SAP particles is set forth in Goldman et al. U.S. Patent No. 5,599,335, incorporated herein by reference.

			Table 10	10			
	Sample 1 (Control) 26)	Sample 2 (Comparative) ²⁷¹	Sample 3 281	Sample 4 29)	Sample 5 301	Sample 6 111	Sample 7 323
	AUL 0.7 psi	AUL 0.7 psi	AUL 0.7 psi	AUL 0.7 psi	AUL 0.7 psi	AUL 0.7 psi	AUL 0.7 psi
1	0	0	0	0	0	0	0
	25.3	14.8	56	26.3	17.8	19.3	13.6
ı —	30.7	50.9	33.2	34.5	23.4	20.4	16.2
	32.1	25.1	37.9	38.8	26.3	21	17.4
	33.8	31.2	43.3	44.1	29.9	20.8	17.6
	34.2	34.3	45.8	45.6	31.8	21.6	19.3
	34.5	36.4	47.6	46.2	32.4	21.7	20.1
	35.2	40	1.64	47.6	33.6	22.3	20.5
	35.2	42.3	49.7	48	35.6	22.8	21.7
	15	115	368	685	707	534	026

Standard, commercial SAP, i.e., neutralized poly(AA), 75% DN, available as A2300, from Chemdal, Corp., Palatine, IL;

27) Comparative sample containing a dry blend of 55% by weight unneutralized poly(vinylamine) particles and 45% by weight unneutralized poly(AA) particles;

20) Multicomponent SAP particles of the present invention, containing 55% unneutralized poly(vinylamine) and 55% poly(AA), prepared in a KitchenAid mixer in accordance with Example 12;

23) Multicomponent SAP particles of the present invention, containing 55% unneutralized poly(vinylamine) and 45% poly(AA), prepared in accordance with Example 12;

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Multicomponent SAP particles of the present invention, containing 55% unneutralized poly(vinylamine) and 45% poly(AA), prepared in accordance with Example 18;

Multicomponent SAP particles of the present invention, containing 55% unneutralized poly(vinylamine) and 45% poly(AA), prepared in accordance with Example 20;

Multicomponent SAP particles of the present invention, containing 55% unneutralized poly(vinylamine) and 45% poly(AA), prepared in accordance with Example 21; and

131 in x 10-7 cm3sec/g.

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The data summarized in Table 10 shows a substantial improvement in AUL at 0.7 psi and SFC for multicomponent particles of the present invention in comparison to a control SAP and a comparative dry blend of SAP particles. Accordingly, a present multicomponent SAP particle has an SFC value of at least about 150 x 10^{-7} cm³sec/g, and preferably at least about 250 x 10^{-7} cm³sec/g. To achieve the full advantage of the present invention, the SFC value is at least about 350 x 10^{-7} cm³sec/g, and can range to greater than 1000×10^{-7} cm³sec/g.

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The present multicomponent SAP particles also exhibit excellent diffusion of a liquid through and between the particles. FIG. 8 contains plots of Performance Under Pressure (PUP) capacity at 0.7 psi over time for a dry blend of 55% unneutralized poly(vinylamine) and 45% unneutralized poly(Vinylamine) and 45% unneutralized poly(AA), for a standard commercial poly(AA) SAP, and for a present multicomponent SAP. The PUP capacity test is similar to the AUL test, but the SAP particles are allowed to absorb a fluid on demand. The PUP test is designed to illustrate absorption kinetics of an SAP particle.

In contrast, the plots of FIG. 8 illus
trate that the present multicomponent SAP particles
(i.e., 55/45 weight ratio unneutralized poly(vinylamine)/poly(AA) particles prepared using a Brabender
extruder in accordance with Example 12 and annealed
for 1 hour at 125°C) essentially attain their absorptive capacity after 1 hour, and have attained
their absorptive capacity after 3 hours. The plots
show that after 3 hours, the PUP capacity of the dry

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blend has not been attained. The present multicomponent SAP particles, therefore, demonstrate a faster absorption of liquids, and a better diffusion rate of liquids into and through the particles, in addition to an ability to absorb and retain a greater amount of liquids than prior or other SAP products.

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FIG. 8 also shows that a standard poly(AA) attains an absorptive capacity quickly, but does not absorb and retain as much of the electrolyte-containing liquid. Overall, FIG. 8 shows that the present multicomponent SAPs exhibit both a) improved absorption and retention, and b) improved permeability and absorption kinetics. Such results are both new and unexpected in the art.

FIG. 9 contains similar plots again showing improved absorption, retention, permeability, and absorption kinetics for a multicomponent SAP particle identical to those used in FIG. 8, except the particles tested in FIG. 9 were surface coated with $80/20~PG/H_2O$ and heated at $125^{\circ}C$ for 1 hour.

FIGS. 10 and 11 illustrate the improved initial performance under pressure (PUP) capacity rate for multicomponent SAP particles of the present invention. FIG. 10 shows the comparative initial PUP capacity rate for absorbency vs. (time) 1/2 for 16 hours between multicomponent SAP particles containing a 55/45 weight ratio of poly(vinylamine) and poly(acrylic acid) surface crosslinked with 80/20 PG/H₂O, a dry blend of poly(vinylamime) and poly(acrylic acid), and a standard 75% neutralized poly(AA) SAP. The plots in FIG. 10 provide a better

measurement of the initial slope of the plots, and, therefore, provides a more meaningful comparison of initial PUP capacity rate.

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The plots in FIG. 10 show a substantially improved initial PUP capacity rate for the multicomponent SAP particles prepared using a KitchenAid mixer (93.2 g/g/hr^{1/2}) compared to a dry blend of SAP particles (40.7 g/g/hr^{1/2}) and to a standard poly(AA) (40.1 g/g/hr^{1/2}). FIG. 11 shows similar results for multicomponent SAP particles prepared in a Brabender extrusion apparatus and annealed for 1 hour at 125°C, i.e., initial PUP capacity of 104.2 g/g/hr^{1/2}.

A multicomponent SAP practice of the present invention, therefore, has an initial PUP capacity rate of at least 50 g/g/hr $^{1/2}$, and preferably at least 70 g/g/hr $^{1/2}$. To achieve the full advantage of the present invention, the multicomponent SAP particle has an initial PUP capacity rate of greater than 90 g/g/hr $^{1/2}$, and preferably greater than 100 g/g/hr $^{1/2}$.

In another test, the free swell rate (FSR) of a present multicomponent SAP particle was compared to the FSR of a standard poly(AA) SAP and 55/45 weight ratio of a poly(vinylamine)/poly-(acrylic acid) dry particle blend. The FSR test, also known as a lockup test, is well known to persons skilled in the art.

The present multicomponent SAP particles had an FSR (in g/g/sec) of 0.49 and 0.48, for 55/45 weight ratio multicomponent SAP particles made in a KitchenAid mixer and a Brabender extruder, respectively. In comparison, a dry blend had an FSR of

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0.10 and a standard neutralized poly(AA) had an FSR of 0.32. Multicomponent SAP particles of the present invention, therefore, have an FSR of greater than 0.35, preferably greater than 0.40, and most preferably greater than 0.45. These data further show the improved ability of the present SAP particles to absorb and retain larger amounts of an electrolyte-containing liquid quickly.

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The multicomponent SAP particles also can be mixed with particles of a second water-absorbing 10 resin to provide an SAP material having improved absorption properties. The second water-absorbing resin can be an acidic water-absorbing resin, a basic water-absorbing resin, or a mixture thereof. The SAP material comprises about 10% to about 90%, 15 and preferably about 25% to about 85%, by weight, multicomponent SAP particles and about 10% to about 90%, and preferably, about 25% to about 85%, by weight, particles of the second water-absorbing resin. More preferably, the SAP material contains 20 about 30% to about 75%, by weight, multicomponent ' SAP particles. To achieve the full advantage of the present invention, the SAP material contains about 35% to about 75%, by weight, the multicomponent SAP particles. The multicomponent SAP particles can be 25 prepared by any of the previously described methods, e.g., extrusion, agglomeration, or interpenetrating polymer network, and can be of any shape, e.g., granular, fiber, powder, or platelets.

The second water-absorbing resin can be any of the previously discussed acidic resins used in the preparation of a multicomponent SAP. The

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second water-absorbing resin, either acidic or basic, can be unneutralized (DN=0), partially neutralized (0<DN<100), or completely neutralized (DN=100). A preferred acidic water-absorbing resin used as the second resin is polyacrylic acid, preferably partially neutralized polyacrylic acid, e.g., DN about 50%, and preferably about 70% up to about 100%. The second water-absorbing resin also can be any of the previously discussed basic resins used in the preparation of a multicomponent SAP. Preferred basic water-absorbing resins used as the second resin are poly(vinylamine) or a poly(dialkylaminoalkyl(meth)acrylamide. Blends of acidic resins, or blends of basic resins, can be used as the second water-absorbing resin. Blends of an acidic resin and a basic resin also can be used as the second water-absorbing resin.

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To illustrate the improved absorption properties demonstrated by an SAP material comprising multicomponent SAP particles and particles of a second water-absorbing resin, mixtures of multicomponent SAP particles and partially neutralized (DN=70) polyacrylic acid (poly(AA)) particles were prepared. As used here and throughout the specification poly(AA) (DN=70) refers to a standard, commercial poly(AA) neutralized about 70% to about 80%, and poly(AA) (DN=0) refers to unneutralized poly(AA). The multicomponent SAP particles contain microdomains of poly(vinylamine) dispersed in poly(AA) (DN=0). The poly(vinylamine)/poly(AA) weight ratio of the multicomponent SAP particles was 55/45. The resulting SAP material was tested for an ability to

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absorb synthetic urine under load at 0.7 psi, in accordance with the previously described method. The results are summarized below:

wt ratio 1)	AUL 0.7 psi (1 hr.)	AUL 0.7 psi (3 hr.)	SFC ($\times 10^{-7}$ cm ³ sec/g)
100/0	26.7	27.1	14
75/25	30.2	30.7	26
50/50	36.7	37.7	72
25/75	40.8	42.6	189
0/100	43.0	46.4	787

10 1) weight ratio of partially neutralized poly(AA) particles to multicomponent SAP particles.

The data presented above shows a substantial improvement in absorption properties achieved by an SAP material comprising a blend of multicomponent SAP particles and particles of a second water-absorbing resin over conventional, partially neutralized poly(AA). The improved results are more clearly demonstrated by comparing the data presented above to the data summarized in the following Table 11, which contains absorption under load data for various mixtures of acidic and basic water-absorbing resins that lack a multicomponent SAP.

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Ī			Table 11	
	Example	Blend Ratio 51	AUL 0.7 psi (1 hr)	AUL 0.7 psi (3 hr)
	1 1)	75/25	27.1	28.9
	1	50/50	30.9	33
	1	25/75	35.9	40.2
. }	2 2)	75/25	26.6	27.3
	2	50/50	28.7	30.3
	2	25/75	26.3	27.3
	. 3 ³⁾	75/25	25.3	26
	3	50/50	21.3	22.8
	3	25/75	15.7	16.4
	4 4)	55/45	37	45.2

Blend of (a) partially neutralized poly(AA) (DN=70) and (b) a mixture containing 55% by weight poly-(vinylamine) and 45% by weight poly(AA) (DN=0);

- Blend of (a) partially neutralized poly(AA) (DN=70) and (b) poly(vinylamine);
- Blend of (a) partially neutralized poly(AA) (DN=70) and (b) poly(AA) (DN=0);
- 20 4) Blend of (a) poly(vinylamine) and (b) poly(AA) (DN=0); and
 - 5) Weight ratio of (a) to (b) in each blend.

Table 12 contains additional AUL data at 0.7 psi showing the substantially improved absorption properties and SFC for blends containing particles of a multicomponent SAP. In particular, the data in Table 12 shows that an SAP material comprising a blend of multicomponent SAP particles and particles of a second water-absorbing resin (i.e., Samples 5-7) greatly outperformed a standard

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poly(AA) absorbent resin (i.e., Sample 1) and a dry blend of water-absorbing resins (i.e., Samples 2 and 3). The blend of multicomponent SAP particles and particles of a second water-absorbing resin also performed well compared to an absorbent containing 100% multicomponent SAP particles.

				Table 12				
Time (min)	Sample 1 (control) 26)	Sample 2 (compara- tive) 27)	Sample 3 (compara- tive) 34)	Sample 4 ²⁸⁾ (compara- tive)	Sample 5 35)	Sample 6 ¹⁶⁾	Sample 7 rt 7	Sample 8 38)
0	0	0	0	0	0	, 0	0	0
5	25.3	14.8	16.4	26	21.7	28.3	27.5	24.4
10	30.7	20.9	23.5	33.2	26.8	34.7	33.6	30.2
15	32.1	25.1	26.8	37.9	30.4	37.8	36.2	32.8
30	33.8	31.2	31.2	43.3	36.9	42.5	39.8	36.5
45	34.2	34.3	33.4	45.8	39.5	44.6	41.9	38.1
09	34.5	36.4	34.8	47.6	42.7	45.9	43.3	38.9
120	35.2	40.0	36.1	49.1	48.7	48.2	46.7	40.1
180	35.2	42.3	37.3	49.7	50.1	50.4	48.4	46.4
SFC	15	115	59	368	194	207	244	179

Comparative sample containing a dry blend of 25% poly(AA) (DN=70), 41.5% poly(vinylamine), and 33.5% poly(AA) (DN=0);
35) SAP material

SAP material containing 10% poly(vinylamine) and 90% multicomponent SAP containing 55% poly(vinylamine) and 45% poly(AA), prepared in accordance with Example 12;
36) SAP material containing 10% and 10% and

SAP material containing 10% poly(AA) (DN=0) and 90% multicomponent SAP containing 55% poly(vinylamine) and poly(AA), prepared in accordance with Example 12; 458

poly(vinylamine) and 45% poly(AA), prepared in accordance with Example 12; Blend of 25% poly(AA) (DN=70) and 75% multicomponent SAP containing 55% poly(vinylamine) and 40% poly(AA), SAP material containing 11% poly(vinylamine), 9% poly(AA) (DN=0), and 80% multicomponent SAP containing

prepared in accordance with Example 12.

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tion properties of an SAP material comprising a blend of (a) multicomponent SAP particles and (b) particles of a second water-absorbing resin, FIG. 12 contains plots of absorbance (g/g), both under load and not under load, for various combinations of poly(AA) (DN=70) and a multicomponent SAP containing 55% poly(vinylamine) dispersed in 45% poly(AA) (DN=0). The combinations tested in FIG. 12, which contain multicomponent SAP particles, outperformed the combinations tested in FIG. 13, which contain a blend of poly(AA) (DN=70), poly(AA) (DN=0), and poly(vinylamine) particles.

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FIGS. 14-17 contain plots of absorbance 15 (q/q) vs. time for various SAP materials and dry blends. FIG. 14 illustrates the absorption properties for a dry blend of poly(AA) (DN=70), poly-(vinylamine), and poly(AA) (DN=0). The results in FIG. 14 are inferior to the results summarized in FIG. 15, which illustrate the absorption properties 20 for an SAP material containing 80% multicomponent SAP, 11% poly(vinylamine), and 9% poly(AA) (DN=70). FIGS. 16 and 17 also show improved absorption properties for a blend of 90% multicomponent SAP and 10% 25 poly(vinylamine) (FIG. 16) and for a blend of 90% multicomponent SAP and 10% poly(AA) (DN=0) (FIG. 17).

FIGS. 18 and 19 show that the present superabsorbent materials exhibit excellent permeability and absorption kinetics, in addition to excellent liquid absorption and retention. The plots in FIGS. 18 and 19 illustrate performance properties for a superabsorbent material containing,

by weight, 75% poly(AA) (DN=70) particles and 25% multicomponent SAP particles (55/45, by weight, poly(vinylamine/poly(AA) (DN=0). This superabsorbent material had an SFC of 34.4 x 10⁻⁷ cm³sec/g. FIG. 18 contains a plot of PUP at 0.7 psi over time. FIG. 18 demonstrates that a present superabsorbent material essentially attains its maximum absorption capacity after one hour (24.02 g/g). After 3 hours, the absorptive capacity was 24.74 g/g. After 16 hours, the absorptive capacity was 26.90 g/g.

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The data presented above illustrates that a present SAP material has an SFC of greater than 15 x 10⁻⁷ cm³ sec/g, and typically greater than 20 x 10⁻⁷ cm³ sec/g. Preferred embodiments have an SFC about 30 x 10⁻⁷ cm³ sec/g or greater, for example, up to about 800 x 10⁻⁷ cm³ sec/g. In particular, an SAP material containing 25% multicomponent SAP particle and 75% poly(AA) (DN=70) particles has an SFC of 34.4 cm³ sec/g. An SAP material containing 75% multicomponent SAP particles and 25% poly(AA) - (DN=70) has an SFC of 189 cm³ sec/g.

FIG. 19 illustrates the initial PUP capacity rate for absorbency vs. $(time)^{1/2}$ over 4 hours for a present SAP material. The plot in FIG. 19 demonstrates an improved initial PUP capacity rate of 45.5 g/g 1 hr^{1/2} for the superabsorbent material. A standard poly(AA)(DN=70) has an initial PUP capacity rate of 40.7 g/g 1 hr^{1/2}.

To further illustrate that the present multicomponent SAP particles and superabsorbent materials containing multicomponent SAP particles,

(a) have an improved ability to absorb liquids faster, (b) have a better liquid diffusion rate, and

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- (c) have an improved ability to absorb and retain liquids, laboratory diaper cores containing the present multicomponent SAP particles were prepared and compared to laboratory diaper cores containing a conventional SAP and to commercially available diapers. In particular, the following the diaper cores were prepared:
- Core A 100% poly(AA) (DN=70)
- Core B 100% multicomponent SAP particles containing 55% poly(vinylamine) and 45% poly(AA)-(DN=0), by weight,
 - Core C 16.5% multicomponent SAP (as in Core B),
 33.5% poly(AA) (DN=70), and 50% fluff pulp,
 by weight,
- 15 Core D 23.3% multicomponent SAP (as in Core B),
 46.7% poly(AA)(DN=70) and 30% fluff pulp,
 by weight,

 - Core F 46.7% multicomponent SAP (as in Core B), 23.5% poly(AA) (DN=70) and 30% fluff pulp, by weight,
- Core G1 27.5% poly(vinylamine), 22.5% poly(AA)
 (DN=0), and 50% fluff pulp, by weight,
 - Core G2 identical to Core G1 except the multicomponent SAP was surface crosslinked with 500 ppm EGDGE,
- Core H1 38.5% poly(vinylamine), 31.5% poly(AA)30 (DN=0), and 30% fluff pulp, by weight,

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Core H2 - identical to Core H1 except the multicomponent SAP was surface-crosslinked with 500 ppm EGDGE.

Cores A and B are referred to as "pulpless" cores, i.e., the cores contain 100% of an SAP. Typically, commercial diapers contain 45% to 60% by weight of a pulp to achieve rapid absorption of a liquid. Diaper Cores A through H2 were compared to one another, and to other laboratory cores and commercial diapers, to illustrate the improved perme-10 ability and absorption kinetics, and improved liquid absorption and retention, provided by a diaper having a core that contains multicomponent SAP particles of the present invention, either as the sole SAP, or as a component in a superabsorbent material. 15 Present day diapers generally consist of a topsheet made from a nonwoven material that is in contact with the skin of the wearer, an acquisition layer below (i.e., opposite the skin of wearer) the topsheet, a core that is below the acquisition 20 layer, and a backsheet below the core. This construction is well known in the industry. In a preferred embodiment, the present diaper consists essentially of a topsheet, a core, and a backsheet, i.e., an acquisition layer is not present. As 25 illustrated below, the improvements provided by present multicomponent SAP particles, or superabsorbent material, permit an acquisition layer to be omitted from a disposable diaper. Such a result is both new and unexpected in the art in that an expen-30 sive acquisition layer can be omitted, the diaper is

lighter and thinner, and absorptive properties are not adversely affected.

Cores A through H2, and the other laboratory cores referred to herein, were prepared using a conventional laboratory procedure as follows:

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A laboratory core-forming unit comprising a two-chamber vacuum system forms an airlaid fluff pulp-absorbent composite matrix to produce a 12 cm x 21 cm diaper core. The core-forming unit comprises a roller brush on a variable-speed laboratory motor, a fiber distribution screen in close proximity to the brush, a forming screen on an adjustable damper, and a vacuum system capable of supplying a consistent and continuous negative pressure between 8 and 15 inches of water.

The core-forming unit is contained such that the vacuum pulls the fibers and granular material from an adjustable introduction slide, through the rotating brush and distribution screen, directly onto the forming screen. The vacuum exhaust is recirculated through the inlet of the formation slide, thereby controlling the temperature and humidity of the operation.

When forming a core, the desired amount of defiberized fluff pulp is evenly disbursed in small pieces onto the brush roller in the upper chamber. In the lower chamber, a rectangular tissue, or top-sheet (21 cm x 12 cm), is placed onto the forming screen. For most cores, the sliding upper chamber lid is partially closed to leave about a one-half inch gap. In the case of a homogeneous pulp/SAP core, the SAP is sprinkled through the gap into the upper chamber immediately after the brush begins

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rotating. In order to achieve a homogeneous distribution, a small amount of SAP is added to the fluff prior to beginning the motor. The amount of time used to introduce the remainder of the SAP varies with the amount of fluff pulp utilized. After the fiber and absorbent polymer material are deposited, the motor is turned off, and the damper unit containing the laboratory core is removed from the lower chamber. The uncompressed core then is placed on a backsheet made from a polymeric film, and put into a compression unit. At this time, another rectangular tissue and a nonwoven coverstock is placed on top of the core. Absorbent cores are compressed for a given amount of time, typically 5 minutes, with a hydraulic press at pressures of between about 5,000 psi and about 10,000 psi, and typically about 7,000 psi, to achieve the desired density. After the 5 minutes, the laboratory-prepared absorbent cores are removed from the press, weighed, and measured for thickness.

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Cores A through H2, and other laboratory cores and commercial diapers, were tested for rewet under a 0.7 psi load, liquid acquisition time, and liquid acquisition rate. The following describes the procedure to determine the acquisition and rewet under load of a hygienic article, like a diaper. These tests exhibit the rate of absorption and fluid retention of a 0.9%, by weight, saline solution, by a hygienic article over 3 to 5 separate fluid insults while under a load of 0.7 psi.

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Apparatus:

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100 ml separatory funnel, configured to deliver a flow rate of 7 ml/sec., or equivalent;
3.642 kg circular weight (0.7 psi) 10 cm diameter, with 2.38 cm ID perspex dose tube through the center of weight;

VWR Scientific, 9 cm filter paper or equivalent;
2.5 kg circular weight (0.7 psi) -- 8 cm diameter;

Digital timer;

10 Electronic balance (accuracy of a 0.01 gram);
 Stopwatch.

Procedure:

1. Preparation

- (a) Record the weight (g) of the hygienic article, e.g., diaper, to be tested;
 - (b) Place hygienic article flat on the bench top, for example, by removing any elastics and/or taping the ends of the article to the bench top;
- 20 (c) Place the 3.64 kg circular weight onto the hygienic article with the opening of the perspex dose tube positioned at the insult point (i.e., 5 cm toward the front from the center).

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2. Primary Insult and Rewet Test

Measure 100 ml of 0.9% NaCl solution (a) (i.e., 0.9% by weight sodium chloride in deionized or distilled water) into separatory funnel. Dispense the NaCl solution 5 into the perspex tube of the weight at a flow rate of 7 ml/sec and start the timer immediately. Stop the timer when all of the NaCl solution has completely disappeared from the surface of the hygienic 10 article at the base of the perspex tube. Record this time as the primary acquisition time (sec). After 10 minutes have elapsed, remove the (b) weight and conduct the rewet test proce-15 dure: Weigh a stack of 10 filter papers, (i) record this value (dry weight). Place the filter papers over the (ii) insult point on the hygienic arti-20 cle. Set the timer for 2 minutes. Place the 2.5 kg weight onto the filter papers and start timer immediately. After 2 minutes have elapsed, re-(iii) 25 move the weight and reweigh the filter papers (wet weight). Subtract the dry weight of the filter papers from the wet weight, this is the rewet value. Record 30 this value as the primary rewet value (g).

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3. Secondary Insult and Rewet Test

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Place the 3.64 kg weight back onto the hygienic article in the same position as before. Repeat step 2a using 50 ml NaCl solution (recoding the absorption time as the secondary acquisition time) and steps 2b (i)-(iii) using 20 filter paper (recording the rewet values as the secondary rewet).

10 4. Tertiary, and additional, Insult and Rewet Tests

(a) Place the load back onto the diaper in the same position as before. Repeat step 2a using 50 ml of NaCl solution (recording the absorption time as the tertiary acquisition time) and steps 2b (i)-(iii) using 30 filter paper (recording the rewet value as the tertiary or subsequent rewet).

The following FIGS. 20-29 illustrate improved diapers that contain multicomponent SAP particles, or that contain superabsorbent materials, of the present invention.

FIG. 20 contains plots of acquisition time vs. number of insults with 0.9% aqueous saline, under a 0.7 psi load, for diapers containing Cores A and B, a core containing 50% of a multicomponent SAP and 50% fluff (Core N), a comparative core containing 50% poly(AA) (DN=70) and 50% fluff (Core I), a core identical to Core I, but absent an SAP (Core J), and a core identical to Core J but containing

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twice the amount of fluff as Core J (Core K). In FIG. 20, Cores B and N are cores of the present invention. Cores A, I, J, and K are comparative cores.

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Cores B and N exhibited an excellent ability to acquire 0.9% saline under a 0.7 psi load.

Cores J and K acquired the saline slowly, especially during rewetting. Core I represents a standard core containing 50% SAP, and has a higher acquisition time than Cores B or C. The acquisition time for Core A could not be measured beyond the third insult because acquisition was very slow.

rIG. 21 illustrates the acquisition time under a 0.7 psi load for Cores I and N and for various commercial diapers. FIG. 21 shows that Core N, a core of the present invention, significantly outperforms both comparative laboratory cores (Core I) and commercial diapers with respect to acquisition time of 0.9% saline under a 0.7 psi load. FIG. 22 illustrates that a core of the present invention, i.e., Core N, has a greater acquisition rate at 0.7 psi than commercial diapers and comparative laboratory cores containing poly(AA) (DN=70) (i.e., acquisition rate is greater than 2 ml/sec for an initial 100 milliliter insult and four subsequent 50 milliliter insults with 0.9% saline).

FIG. 23 contains acquisition times for Cores B, D, and F, for a comparative core containing 70% poly(AA) (DN=70) and 30% fluff (Core L), and for a core containing 70% multicomponent SAP particles and 30% fluff (Core M). Cores B, D, F, and M of the present invention significantly outperformed Core L with respect to acquisition time. Core L could not

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be tested for the fifth insult because the acquisition time was too great.

FIG. 24 similarly compared Cores C, E, I, and N. All cores contained 50% SAP, and Cores C, E, and N of the present invention significantly outperformed comparative Core I. FIG. 25 contains similar plots for cores containing 70% SAP. Cores D, E, and M significantly outperformed comparative Core L with respect to acquisition time.

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time and acquisition rate, and show that at both a 70% SAP loading of the core (FIGS. 26 and 27) and at a 50% SAP loading of the core (FIGS. 28 and 29), the cores of the present invention, i.e., cores G1, G2, H1, H2, M, and N, significantly outperformed comparative cores I and L.

Overall, the data presented in FIGS. 20-29 demonstrate that a diaper core of the present invention maintains a flat, essentially constant, or surprisingly a decreased, acquisition time over five insults, whereas prior cores demonstrate an increased acquisition time as the number of insults increase. The data also shows an unexpected faster acquisition rate as the number of insults increases, i.e., an acquisition rate for a subsequent insult is greater than for a previous insult. Such results are unexpected because prior cores exhibit a decrease in acquisition rate as the number of insults increase. The present cores, therefore, have second acquisition rates that are at most 20% slower than a first acquisition rate, and typically are 1%-20% slower, are equal to, or are greater than the first acquisition rate. The practical result of these

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improved properties is a core having a greatly improved ability to prevent leakage in gush situations and in rewet situations, even in the absence of acquisition layers.

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The data also shows that significant improvements in liquid absorption, both with respect to kinetics and retention, are observed if the standard poly(AA) (DN=70) presently used in cores is completely replaced by multicomponent SAP particles, or is replaced by a superabsorbent material of the present invention, i.e., a composition containing multicomponent SAP particles and a second waterabsorbing resin, such as poly(AA) (DN=70).

The improved results demonstrated by a core of the present invention also permit the thickness of the core to be reduced. Typically, cores contain 50% or more fluff or pulp to achieve rapid liquid absorption while avoiding problems like gel blocking. The present cores, which contain a multicomponent SAP particles, acquire liquids sufficiently fast to avoid problems, like gel blocking, and, therefore, the amount of fluff or pulp in the core can be reduced, or eliminated. A reduction in the amount of the low-density fluff results in a thinner core, and, accordingly, a thinner diaper.

Therefore, a core of the present invention can contain at least 50% of an SAP, preferably at least 75% of an SAP, and up to 100% of an SAP. In various embodiments, the presence of a fluff or pulp is no longer necessary, or desired. In each case, the SAP in a present core contains multicomponent SAP particles, in an amount of about 15% to 100% of the SAP. The remaining SAP can be a second water-

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absorbing resin, either basic or acidic. The second water-absorbing resin preferably is not neutralized, but can have a degree of neutralization up to 100%. The multicomponent SAP particles can be admixed with particles of a second water-absorbing resin for introduction into a diaper core. Alternatively, the diaper core can contain zones of multicomponent SAP particles and zones of a second water-absorbing resin.

In addition to a thinner diaper, the present cores also allow an acquisition layer to be omitted from the diaper. The acquisition layer in a diaper typically is a nonwoven or fibrous material, typically having a high degree of void space of "loft," that assists in the initial absorption of a liquid. The present cores acquire liquid at a sufficient rate such that diapers free of an acquisition layers are practicable.

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Many modifications and variations of the
invention as hereinbefore set forth can be made
without departing from the spirit and scope thereof
and, therefore, only such limitations should be
imposed as are indicated by the appended claims.

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WHAT IS CLAIMED IS:

- 1. A multicomponent superabsorbent particle comprising at least one microdomain of at least one basic water-absorbing resin dispersed in a continuous phase of at least one acidic water-absorbing resin.
- 2. The particle of claim 1 wherein the basic resin comprises a strong basic resin, and the acidic resin comprises a strong acidic resin, a weak acidic resin, or a mixture thereof.
- 3. The particle of claim 1 wherein the basic resin comprises a weak basic resin, and the acidic resin comprises a strong acidic resin, a weak acidic resin, or a mixture thereof.
- 4. The particle of claim 1 having a weight ratio of acidic resin to basic resin of about 90:10 to about 10:90.
- 5. The particle of claim 1 containing about 50% to 100%, by weight, of basic resin plus acidic resin.
- 6. The particle of claim 1 wherein the particle is about 10 to about 10,000 microns in diameter.

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- 7. The particle of claim 1 wherein the basic resin is annealed at a temperature of about 65°C to about 150°C for about 20 minutes to about 16 hours.
- 8. The particle of claim 1 wherein the basic resin is surface crosslinked with up to about 1% by weight of the particle of a surface crosslinking agent.
- 9. The particle of claim 8 wherein the surface crosslinking agent is selected from the group consisting of
- (a) a dihalide or a disulfonate ester having the formula

$$Y = (CH_2)_p = Y_r$$

wherein p is an integer 2 to 12 and Y, independently, is halo, tosylate, mesylate, an alkyl sulfonate ester, or an aryl sulfonate ester;

- (b) a multifunctional aziridine;
- (c) a multifunctional aldehyde, and acetals and bisulfites thereof;
 - (d) a halohydrin;
 - (e) a multifunctional epoxy compound;
- (f) a multifunctional carboxylic acid containing 2 to 12 carbon atoms, and methyl and ethyl esters, acid chlorides, and anhydrides derived therefrom;
 - (g) an organic titanate;
 - (h) a melamine resin;

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- (i) a hydroxymethyl urea;
- (j) a multifunctional isocyanate; and
- (k) mixtures thereof.
- 10. The particle of claim 1 wherein the particle is surface crosslinked with up to about 10,000 ppm of a surface crosslinking agent.
- 11. The particle of claim 9 wherein the surface crosslinking agent is selected from the group consisting of a polyhydroxy compound, a metal salt, a quaternary ammonium compound, a multifunctional epoxy compound, an alkylene carbonate, a polyaziridine, a haloepoxy, a polyamine, a polyisocyanate, and mixtures thereof.
- 12. The practice of claim 1 wherein the particle is annealed at a temperature of about 65°C to about 150°C for about 20 minutes to about 16 hours.
- 13. The particle of claim 1 wherein the basic resin has about 75% to 100% basic moieties present in a free base form.
- 14. The particle of claim 1 wherein the basic resin is lightly crosslinked.
- 15. The particle of claim 1 wherein at least 6% of the monomer units comprising the basic resin are basic monomer units.

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- basic resin is selected from the group consisting of a poly(vinylamine), a poly(dialkylaminoalkyl (meth)-acrylamide), a polymer prepared from the ester analog of an N-(dialkyamino(meth)acrylamide), a polyethylenimine, a poly(vinylguanidine) a poly(allylguanidine), a poly(allylamine), a poly(dimethyldialkylammonium hydroxide), a guanidine-modified polystyrene, a quaternized polystyrene, a quaternized polystyrene, a quaternized polystyrene, a quaternized polycomplamine), and mixtures thereof.
 - 17. The particle of claim 1 wherein the acidic resin contains a plurality of carboxylic acid, sulfonic acid, sulfuric acid, phosphonic acid, or phosphoric acid groups, or a mixture thereof.
 - 18. The particle of claim 1 wherein the acidic resin has about 75% to 100% acid moieties present in the free acid form.
 - 19. The particle of claim 1 wherein at least 10% of the monomer units comprising the acidic resin are acidic monomer units.
 - 20. The particle of claim 1 wherein the acidic resin is lightly crosslinked.

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- 21. The particle of claim 1 wherein the acidic resin is selected from the group consisting of polyacrylic acid, a hydrolyzed starch-acrylonitrile graft copolymer, a starch-acrylic acid graft copolymer, a saponified vinyl acetate-acrylic ester copolymer, a hydrolyzed acrylonitrile polymer, a hydrolyzed acrylonitrile polymer, a hydrolyzed acrylamide copolymer, an ethylene-maleic anhydride copolymer, an isobutylene-maleic anhydride copolymer, a poly(vinylphosphonic acid), a poly-(vinylsulfonic acid), a poly(vinylphosphoric acid), a poly(vinyl-sulfuric acid), a sulfonated polystyrene, a poly(aspartic acid), a poly(lactic acid), and mixtures thereof.
- 22. The particle of claim 1 wherein the basic resin comprises a poly(vinylamine), a poly-(dialkylaminoalkyl (meth)acrylamide), a poly-(vinylguanidine), a polyethylenimine, or a mixture thereof, and the acidic resin comprises poly(acrylic acid).
- 23. The particle of claim 22 wherein the poly(dialkylaminoalkyl (meth)acrylamide) comprises poly(dimethylaminoethyl acrylamide), poly(dimethylaminopropyl methacrylamide), or a mixture thereof.
- 24. The particle of claim 22 wherein the poly(acrylic acid) resin further contains strong acid moieties.

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- 25. The particle of claim 1 comprising a plurality of microdomains of at least one basic water-absorbing resin.
- 26. An article comprising a multicomponent superabsorbent particle of claim 1.
- 27. A method of absorbing an aqueous medium comprising contacting the medium with a plurality of particles of claim 1.
- 28. A method of claim 27 wherein the aqueous medium contains electrolytes.
- 29. A method of claim 27 wherein the electrolyte-containing aqueous medium is selected from the group consisting of urine, saline, menses, and blood.
- 30. A multicomponent superabsorbent particle comprising at least one microdomain of at least one acidic water-absorbing resin dispersed in a continuous phase of at least one basic water-absorbing resin.
- 31. The particle of claim 30 comprising a plurality of microdomains of at least one acidic water-absorbing resin.

- 32. A method of absorbing an aqueous medium comprising contacting the medium with a particle of claim 30.
- particle comprising at least one microdomain of at least one basic water-absorbing resin and at least one microdomain of at least one microdomain of at least one acidic water-absorbing resin dispersed in a continuous phase of a matrix resin.
- 34. The particle of claim 33 comprising a plurality of microdomains of at least one basic water-absorbing resin and a plurality of microdomains of at least one acidic water-absorbing resin.
- 35. The particle of claim 33 comprising 25% to 50%, by weight, of a matrix resin.
- 36. The particle of claim 33 wherein the matrix resin comprises a hydrophilic resin.
- 37. A method of absorbing an aqueous medium comprising contacting the medium with a particle of claim 33.

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- 38. A multicomponent superabsorbent particle comprising at least one microdomain of at least one basic water-absorbing resin in contact with at least one microdomain of at least one acidic water-absorbing resin.
- 39. The particle of claim 38 comprising a plurality of microdomains of at least one basic water-absorbing resin in intimate contact with a plurality of microdomains of at least one acidic water-absorbing resin.
- 40. The particle of claim 38 further comprising at least one microdomain of a matrix resin in an amount of 0% to 50% by weight of the particle.
- 41. The particle of claim 38 consisting essentially of microdomains of the acidic resin and the basic resin.
- 42. A method of absorbing an aqueous medium comprising contacting the medium with a particle of claim 38.

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- 43. A multicomponent superabsorbent particle comprising at least one microdomain of a first water-absorbing resin in contact with at least one microdomain of a second water-absorbing resin.
- 44. The particle of claim 43 comprising a plurality of microdomains of a first water-absorbing resin dispersed in a continuous phase of a second water-absorbing resin.
- 45. The particle of claim 43 in the form of a bead, a granule, a flake, an interpenetrating polymer network, a fiber, an agglomerated particle, a laminate, a powder, a foam, or a sheet.
- 46. The particle of claim 43 having an absorption under load at 0.7 psi of at least about 10 grams of 0.9% saline per gram of particles, after one hour, and at least about 10 grams of 0.9% saline per gram of particles after three hours.
- 47. The particle of claim 43 having a saline flow conductivity value of at least 150 x 10^{-7} cm³sec/g.
- 48. The particle of claim 43 having an initial performance under pressure capacity rate of greater than 50 $g/g/hr^{1/2}$.
- 49. The particle of claim 43 having a free swell rate greater than 0.35 g/g/sec.

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- 50. The particle of claim 43 wherein the first resin comprises a basic water-absorbing resin, and the second resin comprises an acidic water-absorbing resin.
- 51. The particle of claim 43 wherein the first resin comprises an acidic water-absorbing resin, and the second resin comprises a basic water-absorbing resin.
- 52. The particle of claim 43 wherein the first resin comprises an acidic water-absorbing resin, a basic water-absorbing resin, or a mixture thereof and the second resin comprises a matrix resin.
- 53. The particle of claim 43 wherein the first resin comprises an acidic water-absorbing resin, and the second resin comprises a mixture of a matrix resin and a basic water-absorbing resin.
- 54. A multicomponent superabsorbent particle comprising at least one microdomain of an acidic water-absorbing resin in close proximity to at least one microdomain of a basic water-absorbing resin.

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- 55. A superabsorbent material comprising:
- (a) multicomponent superabsorbent particles, wherein each multicomponent superabsorbent
 particle comprises at least one microdomain of a
 first water-absorbing resin in contact with or in
 close proximity to at least one microdomain of a
 second water-absorbing resin, and
 - (b) particles of a second water-absorbing resin selected from the group consisting of an acidic water-absorbing resin, a basic water-absorbing resin, and mixtures thereof.
 - 56. The superabsorbent material of claim 55 wherein the multicomponent superabsorbent particles are present in an amount of about 10% to about 90%, by weight, of the material.
 - 57. The superabsorbent material of claim 55 wherein the multicomponent superabsorbent particles are 0% to 25% neutralized, and the second water-absorbing resin is 0% to 100% neutralized.
 - 58. The multicomponent particles of claim 55 in the form of a bead, a granule, a flake, an interpenetrating polymer network, a fiber, an agglomerated particle, a laminate, a powder, a foam, or a sheet.

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- 59. The multicomponent particles of claim 55 wherein the first resin comprises a basic waterabsorbing resin, and the second resin comprises an acidic water-absorbing resin.
- 55 wherein the first resin comprises an acidic water-absorbing resin, and the second resin comprises a mixture of a matrix resin and a basic water-absorbing resin.
- 61. The superabsorbent material of claim 55 wherein the second water-absorbing resin has a degree of neutralization from 0 to 70.
- 62. The superabsorbent material of claim 55 wherein the second water-absorbing resin comprises an acidic water-absorbing resin.

- 63. The superabsorbent material of claim 62 wherein the acidic water-absorbing resin is selected from the group consisting of polyacrylic acid, a hydrolyzed starch-acrylonitrile graft copolymer, a starch-acrylic acid graft copolymer, a saponified vinyl acetate-acrylic ester copolymer, a hydrolyzed acrylonitrile polymer, a hydrolyzed acrylamide copolymer, an ethylene-maleic anhydride copolymer, an isobutylene-maleic anhydride copolymer, a poly(vinylphosphonic acid), a poly(vinyl-sulfonic acid), a poly(vinylphosphoric acid), a poly(vinylsulfuric acid), a sulfonated polystyrene, a poly(aspartic acid), a poly(lactic acid), and mixtures thereof.
 - 64. The superabsorbent material of claim 55 wherein the second water-absorbing resin comprises a basic water-absorbing resin.
 - 65. The superabsorbent material of claim 64 wherein the basic water-absorbing resin is selected from the group consisting of a poly(vinyl-amine), a poly(dialkylaminoalkyl(meth)acrylamide), a polymer prepared from the ester analog of an N-(dialkylamino(meth)acrylamide), a polyethylenimine, a poly(vinylguanidine), a poly(allylguanidine), a poly(allylamine), a poly(dimethyldialkylammonium hydroxide), a guanidine-modified polystyrene, a quaternized polystyrene, a quaternized polystyrene, a quaternized poly(meth)-acrylamide or ester analog thereof, poly(vinyl-alcohol-co-vinylamine), and mixtures thereof.

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- 66. The superabsorbent material of claim 55 having an absorption under load at 0.7 psi of at least about 20 grams of 0.9% saline per gram of particles, after one hour, and at least about 30 grams of 0.9% saline per gram of particles after three hours.
- 67. The superabsorbent material of claim 55 having a saline flow conductivity value of greater than 15×10^{-7} cm³sec/g.
- 68. The superabsorbent material of claim 55 having an initial performance under pressure capacity rate of greater than 40 g/g/hr $^{1/2}$.
- 69. The superabsorbent material of claim 55 having a free swell rate greater than 0.30 g/g/sec.
- 70. A method of absorbing an aqueous medium comprising contacting the medium with a superabsorbent material of claim 55.
- 71. A method of claim 70 wherein the aqueous medium contains electrolytes.
- 72. A method of claim 71 wherein the electrolyte-containing aqueous medium is selected from the group consisting of urine, saline, menses, and blood.

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- 73. An article comprising superabsorbent material of claim 55.
- 74. A diaper having a core, said core comprising at least 15% by weight of multicomponent superabsorbent particles, wherein each multicomponent superabsorbent particle comprises at least one microdomain of a first water-absorbing resin in contact with or in close proximity to at least one microdomain of a second water-absorbing resin.
- 75. The diaper of claim 74 wherein the core has an acquisition rate for 100 milliliters of 0.9% saline under a load of 0.7 psi greater than two milliliters/second.
- 76. The diaper of claim 75 wherein the core has an acquisition rate for a subsequent 50 milliliters of 0.9% saline of greater than two milliliters/second.
- 77. The diaper of claim 76 wherein the core has an acquisition rate for a second subsequent 50 milliliters of 0.9% saline of greater than two milliliters/second.
- 78. The diaper of claim 74 wherein the core comprises at least 50% by weight multicomponent superabsorbent particles.

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- 79. The diaper of claim 74 wherein the core comprises at least 75% by weight multicomponent superabsorbent particles.
- 80. The diaper of claim 74 wherein the core comprises 100% by weight multicomponent superabsorbent particles.
- 81. The diaper of claim 74 further comprising a topsheet in contact with a first surface of the core, and a backsheet in contact with a second surface of the core, said second core surface opposite from said first core surface.
- 82. The diaper of claim 81 further comprising an acquisition layer disposed between the topsheet and the core.
- 83. The diaper of claim 82 wherein the diaper is free of an acquisition layer.
- 84. A diaper having a core, said core comprising at least 15% by weight of a superabsorbent material of claim 55.
- 85. The diaper of claim 84 wherein the core has an acquisition rate for 100 milliliters of 0.9% saline under a load of 0.7 psi of greater than two milliliters/second, and has an acquisition for a first, second, and third subsequent 50 milliliters of 0.9% saline under a load of 0.7 psi of greater than two milliliters/second.

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- 86. The diaper of claim 85 wherein the core comprises at least 50% by weight of the superabsorbent material.
- 87. The diaper of claim 85 wherein the core comprises 100% by weight of the superabsorbent material.
- 88. The diaper of claim 85 further comprising a topsheet in contact with a first surface of the core, and a backsheet in contact with a second surface of the core, said second core surface opposite from said first core surface.
- 89. The diaper of claim 88 further comprising an acquisition layer disposed between the topsheet and the core.
- 90. The diaper of claim 88 wherein the diaper is free of an acquisition layer.
- 91. A diaper comprising a core, a topsheet for the core, and a backsheet for the core,
 said core having a first acquisition rate for absorbing 100 milliliters of 0.9% saline and having a
 second acquisition rate for absorbing a subsequent
 50 milliliters of 0.9% saline, wherein the second
 acquisition rate is equal to or greater than the
 first acquisition rate.

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- 92. The diaper of claim 91 having a third acquisition rate for absorbing a second subsequent 50 milliliters of 0.9% saline, wherein the third acquisition rate is equal to or greater than the second acquisition rate.
- 93. The diaper of claim 91 having a fourth acquisition rate for absorbing a third subsequent 50 milliliters of 0.9% saline, wherein the fourth acquisition rate is equal to or greater than the first acquisition rate.
- 94. The diaper of claim 91 wherein the diaper is free of an acquisition layer.
- 95. A method of increasing an acquisition rate and decreasing an acquisition time of a diaper core in an absorption of a liquid comprising substituting at least 15% by weight of a superabsorbent polymer present in the diaper core with multicomponent superabsorbent particles, wherein each multicomponent superabsorbent particle comprises at least one microdomain of a first water-absorbing resin in contact with or in close proximity to at least one microdomain of a second water-absorbing resin.

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- 96. A diaper comprising a core, a topsheet for the core, and a backsheet for the core,
 said core having a first acquisition rate for absorbing 100 milliliters of 0.9% saline and having a
 second acquisition rate for absorbing a subsequent
 50 milliliters of 0.9% saline, wherein the second
 acquisition rate is 1% to 20% slower than the first
 acquisition rate.
- 97. The diaper of claim 96 wherein the second acquisition rate is 1% to 10% slower than the first acquisition rate.

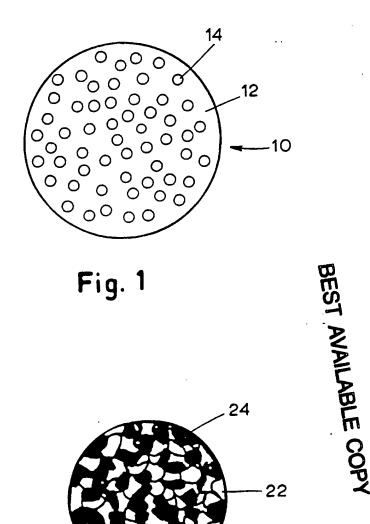


Fig. 2

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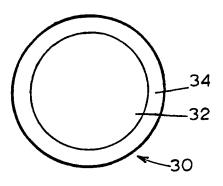


Fig. 3A

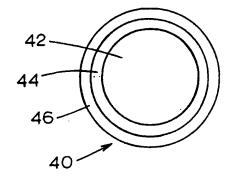


Fig. 3B

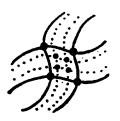


Fig. 5A

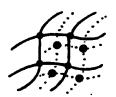
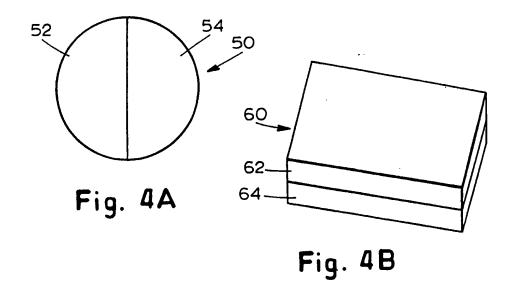
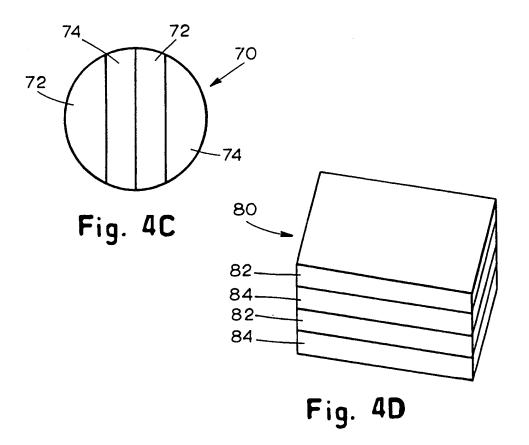
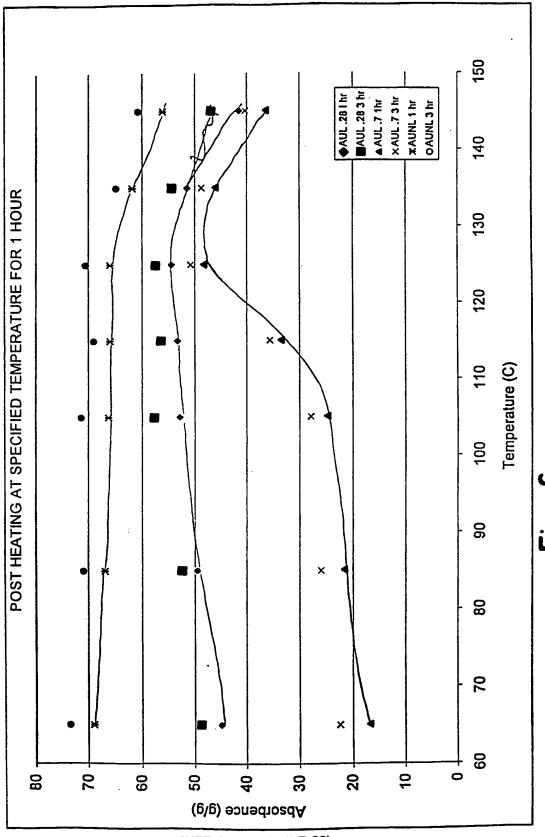


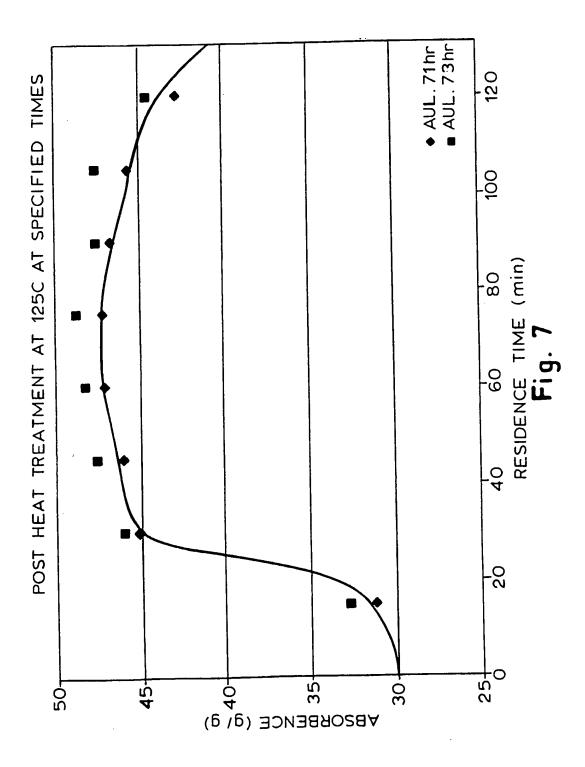
Fig. 5B





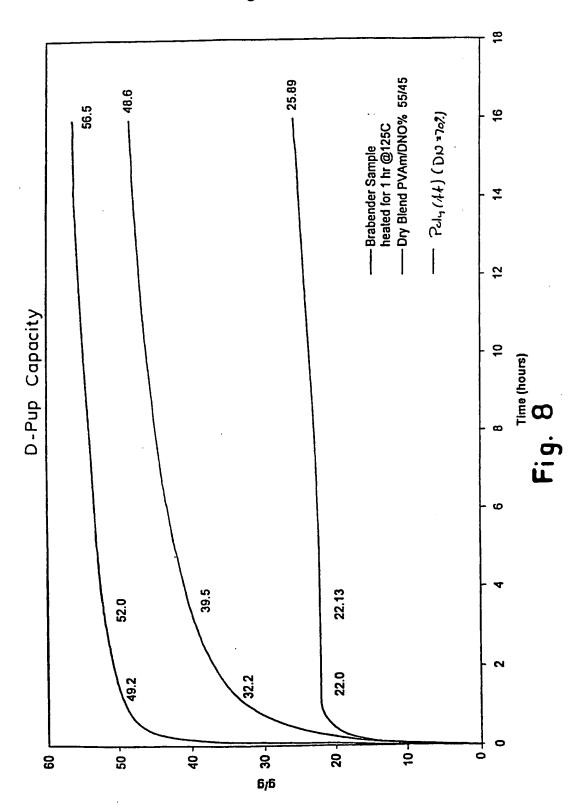


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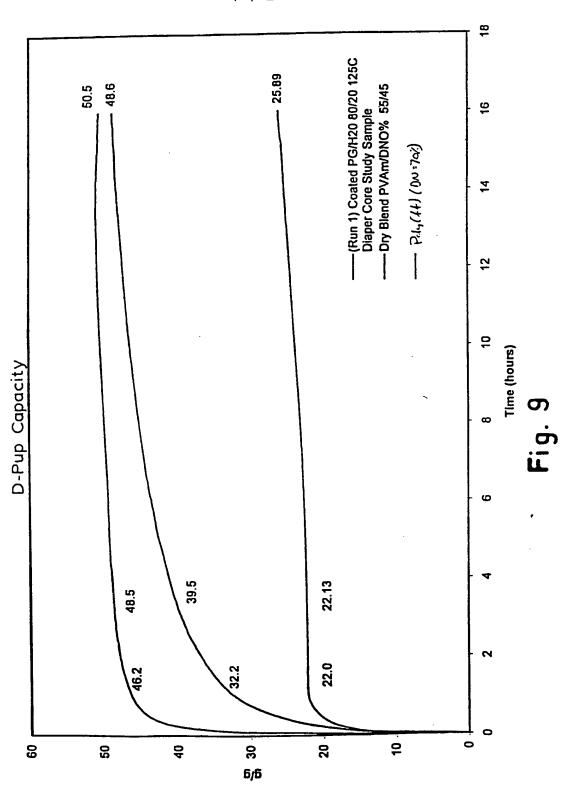
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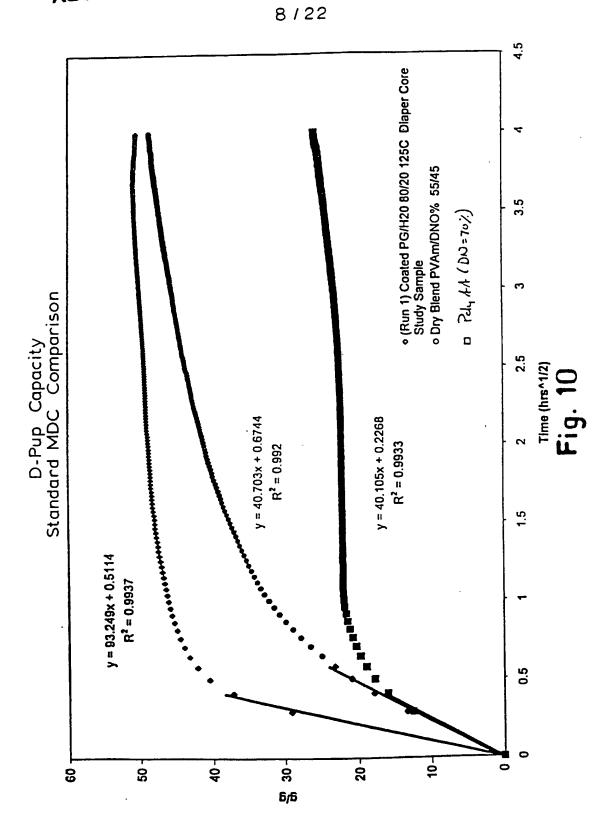




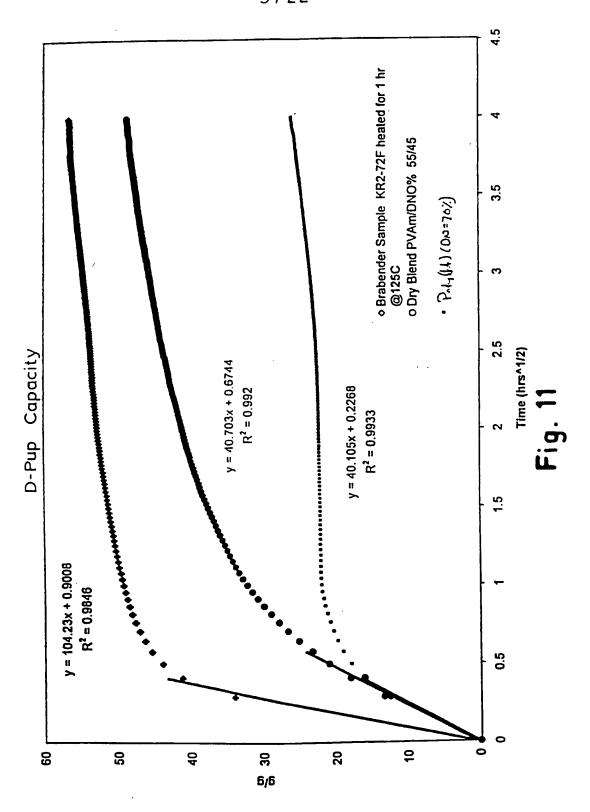
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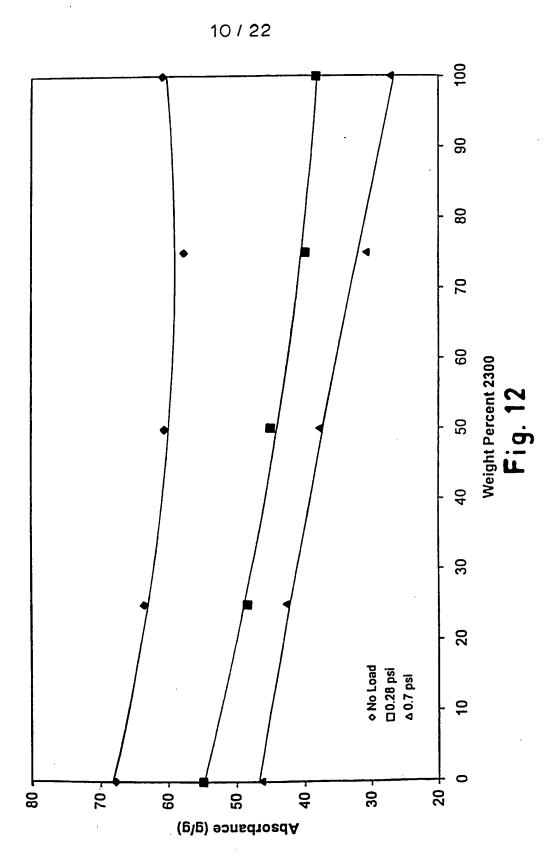


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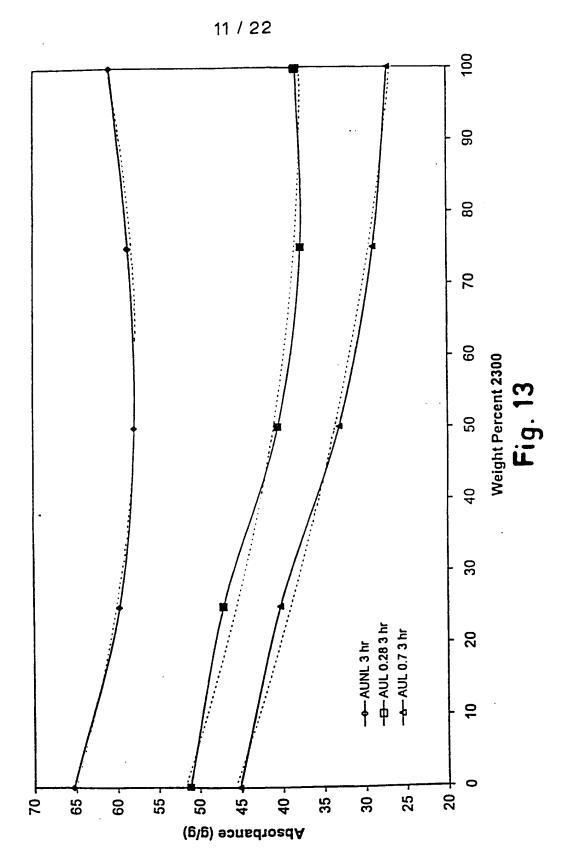


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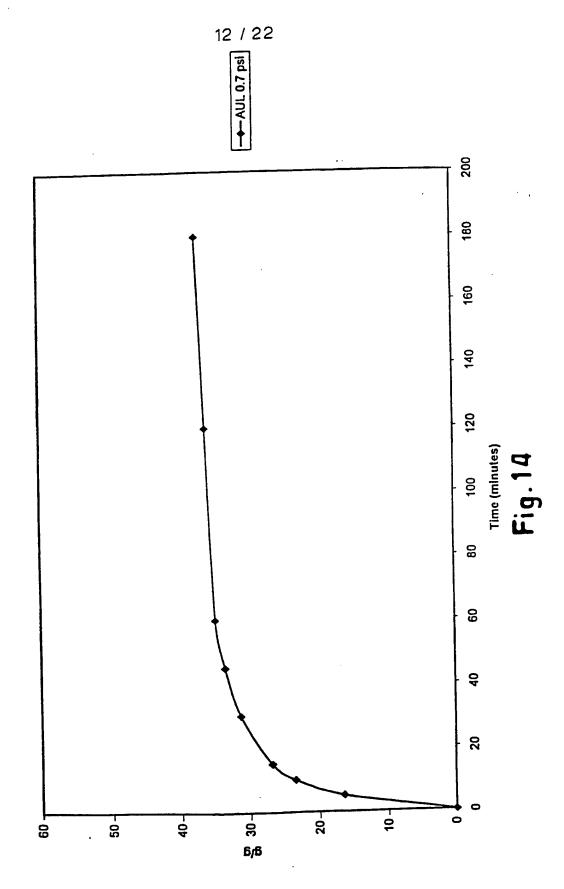
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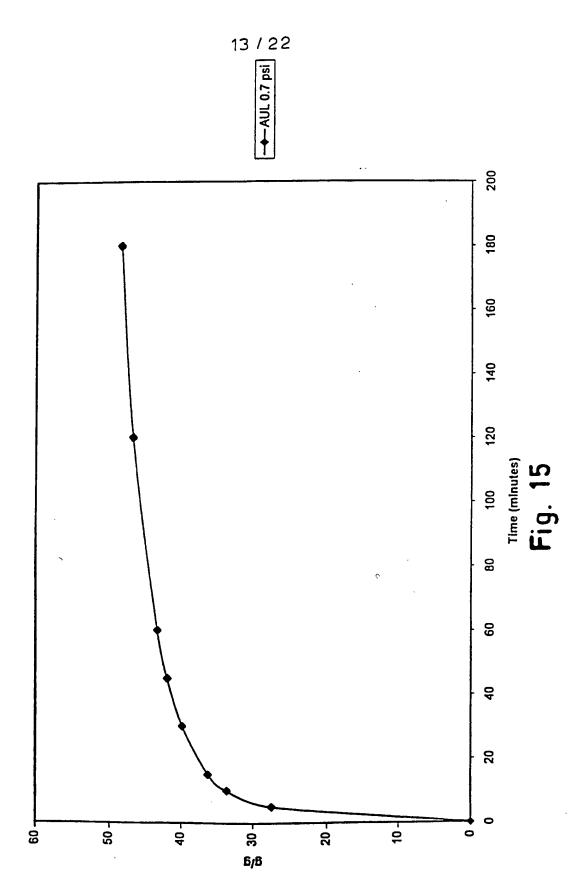
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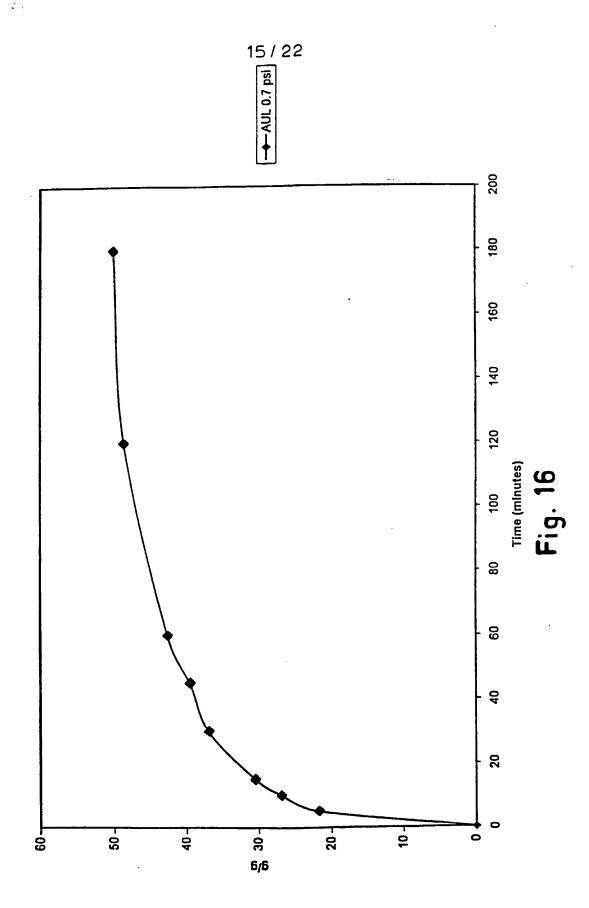
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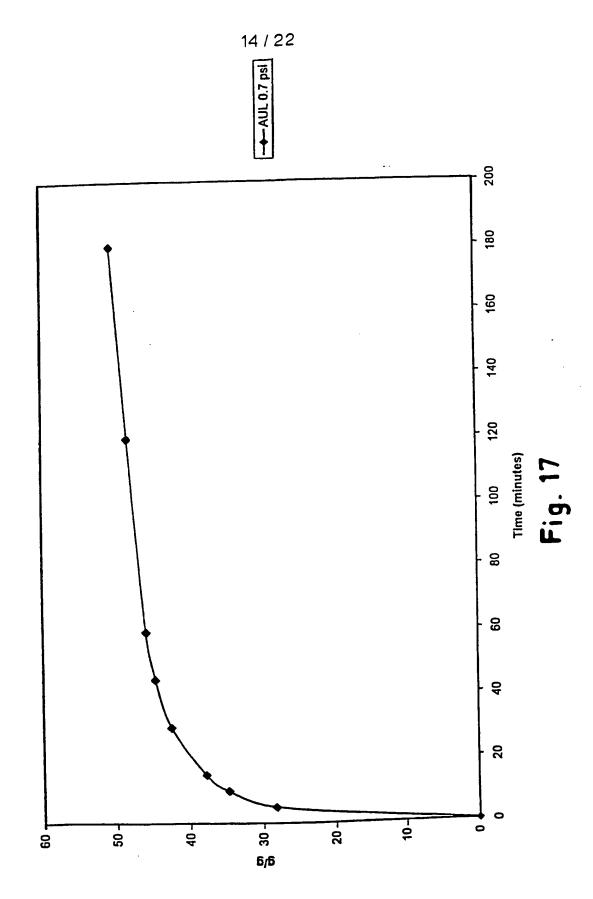
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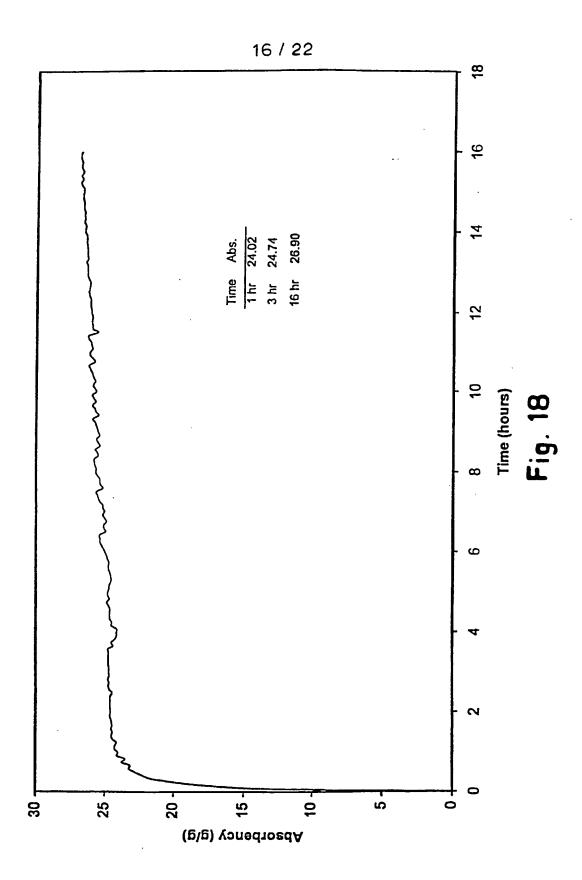
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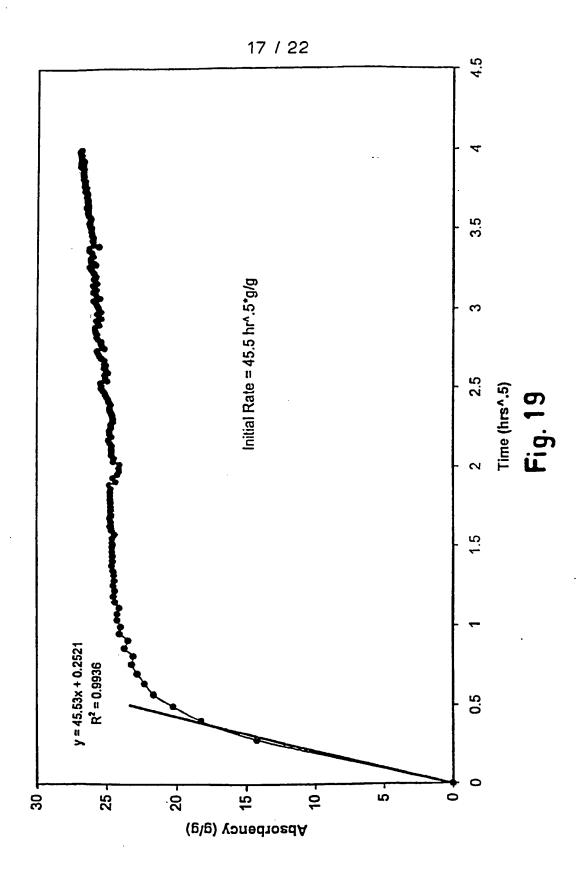


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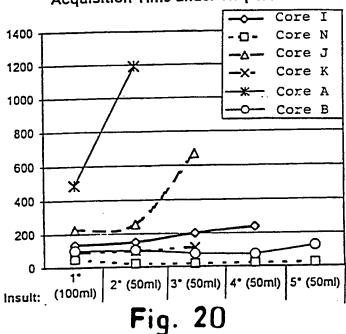




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Time (s)

18 / 22 Acquisition Time under 0.7 psi load



Acquisition Time under 0.7 psi load

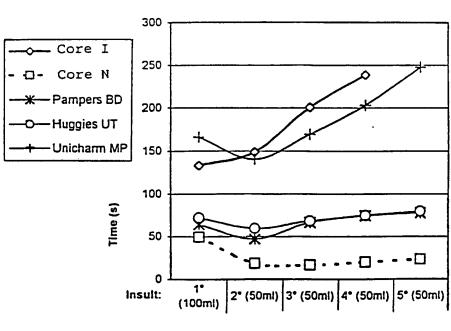


Fig. 21

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Acquisition Rate under 0.7 psi load

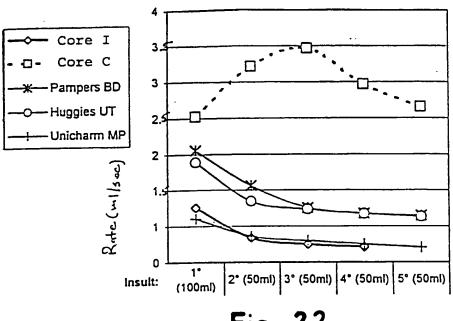


Fig. 22

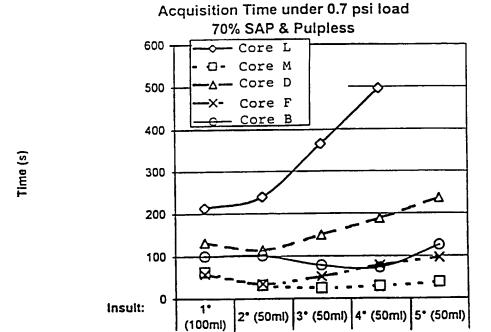


Fig. 23

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20 / 22 Acquisition Time under 0.7 psi load 50% SAP loading

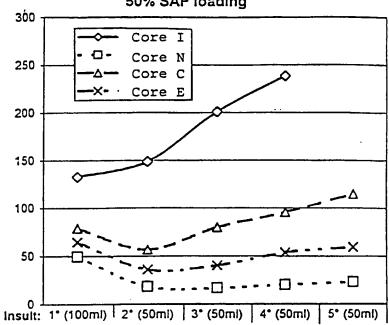


Fig. 24

Acquisition Time under 0.7 psi load 70% SAP loading

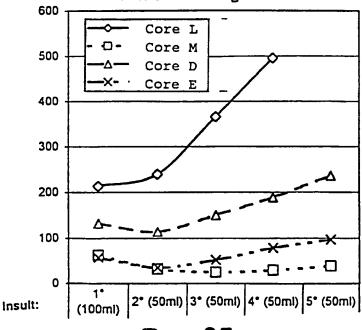


Fig. 25

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Acquisition Time under 0.7 psi load 70% SAP loading

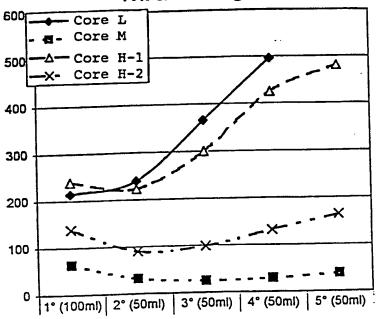


Fig. 26

Acquisition Rate under 0.7 psi load 70% SAP loading

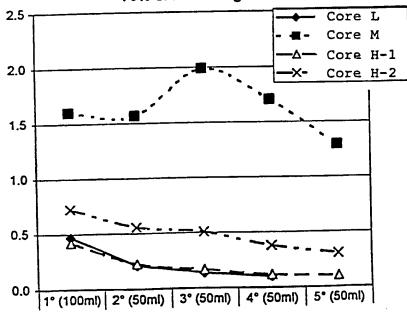


Fig. 27

Rate (ml/s)

Time (s)

Time (s)

22 / 22
Acquisition Time under 0.7 psi load

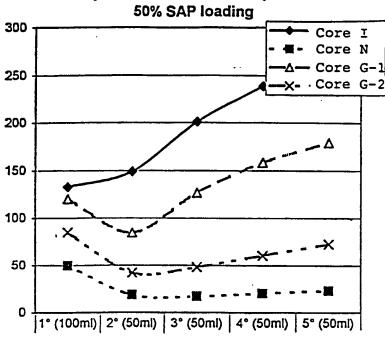
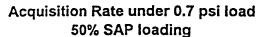


Fig. 28



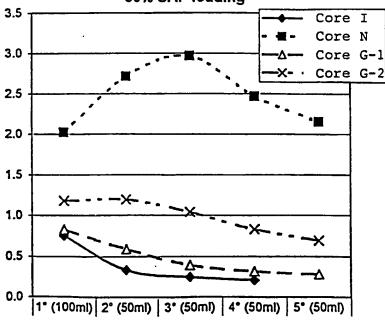


Fig. 29 SUBSTITUTE SHEET (RULE 26)

Rate (ml/s)